Etching

Franssila: Chapters 11, 16, 20, & 21

Peter Hadley

SABRE® PRODUCT FAMILY

Technology: Electrochemical Deposition (ECD)

Solutions: Interconnect, Advanced Memory

http://www.lamresearch.com/products/deposition-products

Lam’s market-leading ALTUS systems combine CVD and ALD technologies to deposit the highly conformal films needed for advanced tungsten metallization applications. Nucleation layer formed using Lam’s Pulsed Nucleation Layer (PNL) ALD process and in-situ bulk CVD fill.

http://www.lamresearch.com/products/deposition-products

Etching

Wet chemical etching
Ion milling
Reactive ion etching
Chemical-Mechanical Polishing

Wet etching

Etchant

Etch stop
(DI water)

etching rate, anisotropy, selectivity

Wet Etching

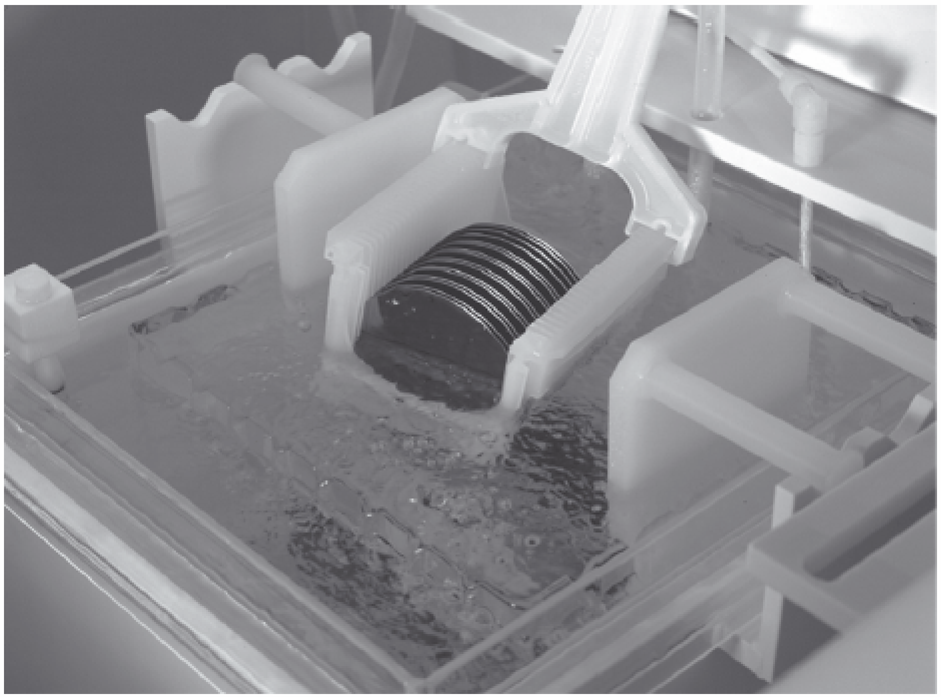

Figure 11.8 Wet etching tank. Courtesy VTT

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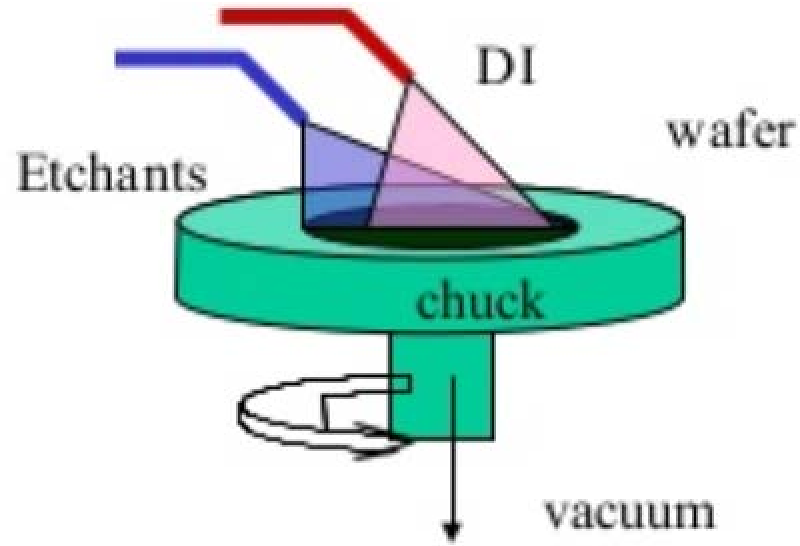


Spray etching

http://www.slideshare.net/gkdelhi8/slide-25-36278815 http://www.cleanroom.byu.edu/wet_etch.phtml

Wet Chemical Etching of Metals and Semiconductors

Etch rate depends on deposited m

A comprehensive list of etchants for over 50 different me specified.

- Aluminum
- Aluminum Gallium Arsenide
- Aluminum Trioxide / Alumina / Sapphire
- Antimony
- Bismuth
- Brass
- Bronze
- Carbon
- Chromium
- Cobalt
- Copper
- Epoxies
- Gallium Arsenide
- Germanium
- Gold
- Hafnium
- Indium
- Indium Gallium Arsenide
- Indium Gallium Phosphide
- Indium Phosphide
- Indium Phosphide Oxide Etchants

Aluminum

>

Concentrations	Etchants	Rate (angstroms/sec)	Temperature/Other
1 : 1	H_2O : HF		
1 : 1 : 1	HCl : HNO_3 : H_2O		
dilute or concentrated	HCl		
	H_3PO_4 : HNO_3 : HAc		
19 : 1 : 1 : 2	H_3PO_4 : HAc : HNO_3 : H_2O	40	
3 : 1 : 3 : 1	H_3PO_4 : HAc : HNO_3 : H_2O	8.7 @ >RT	@ 40 C <4 min/micron
4 : 4 : 1 : 1	H_3PO_4 : HAc : HNO_3 : H_2O	5.6	
15 : 0 : 1 : 1-4	H_3PO_4 : HAc : HNO_3 : H_2O	1500	40 C
8 : 1 : 1	H_3PO_4 : H_2O_2 : H_2O	100	@ 35C
3 : 1 : 5	H_3PO_4 : H_2O : glycerin		
69 : 131	$HClO_4$: HAc		
4 : 1 : 5	HCl : FeCle : H_2O		
	$FeCl_3$: H_2O		100 F
10%	$K_3Fe(CN)_6$	100	
	KOH : $K_3Fe(CN)_6$: $K_2B_4O_7.4H_2O$		
2 : 3 : 12	$KMnO_4$: NaOH : H_2O		
1 : 1 : 3	NH_4OH : H_2O_2 : H_2O		
20%	NH_4SO_4		

Acid safety

Acid Safety

The following is the manual used to train cleanroom personnel about handling and storing acids:

Operating Instructions

Read the MSDS
Know which precautions to take
Dispose of acids properly

http://www.cleanroom.byu.edu/acid_safety.phtml

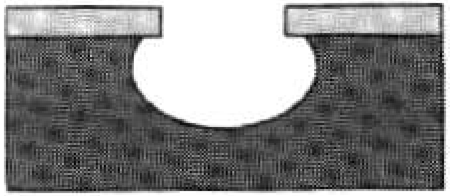
Solvent safety

Solvents used in the IML:

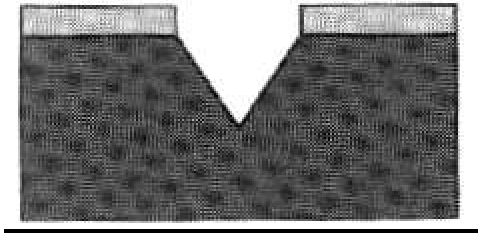
Chemical	Abbreviation	Fire Hazard	Toxicity Hazard	TLV ppm	Odor Threshold	Toxic Effects
Acetone	ACE	Extreme	Low	750	140 ppm (sweet/fruity)	Irritates eyes, nose and throat; headaches; skin dryness
Freon	TF	Low	Low	1000	Variable	Dries skin; light headedness
Isopropyl Alcohol	IPA	Extreme	Low	400	20 ppm (sharp/musty)	Dries skin; irritates eyes, nose and throat; drowsiness
Methyl Isoamylketone	MIAK	Moderate	Extreme	50	0.05 ppm (sweet/sharp)	Irritates eyes, nose and throat; may cause weakness, dizziness, lightheadedness, nausea, vomiting, or kidney damage
Methyl Isobutylketone	MIBK	Extreme	Extreme	50	0.3 ppm (sweet/sharp)	Irritates eyes, nose and throat; may cause weakness, dizziness, lightheadedness, nausea, vomiting, or kidney damage
Methyl Ethylketone	MEK	Extreme	Extreme	200	2-100 ppm (misty)	Irritation of eyes and nose; intoxication, headache, and dizziness
Ethyl Lactate	Positive Photo Resist	Moderate	Low	None	None (fruity/ester)	Combustible liquid; skin, eye, respiratory irritant; nervous system toxin
Propylene Glycol Monomethyl Ether Acetate	PGMEA	Moderate	Low	None	Very low (slightly sweet odor)	Irritant; may cause itching, redness and burns to skin; ingestion may cause diarrhea, kidney and liver damage

http://www.cleanroom.byu.edu/solvent_safety.phtml

Isotropic and anisotropic etching



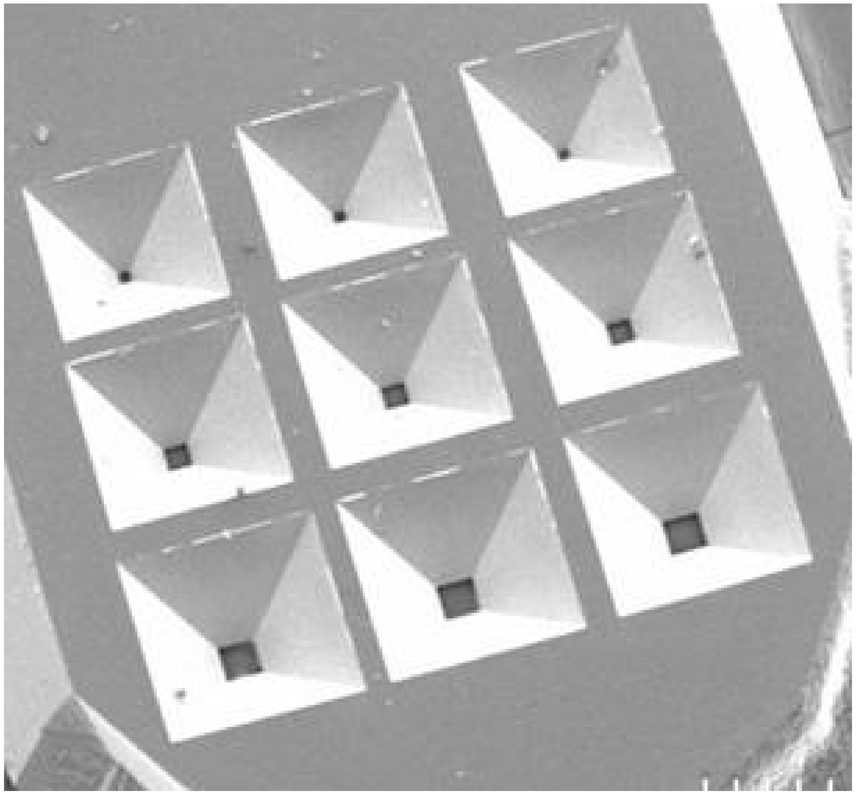
Isotropic



Anisotropic

http://mmadou.eng.uci.edu/Book/Q_Chap4.htm

KOH etching of silicon



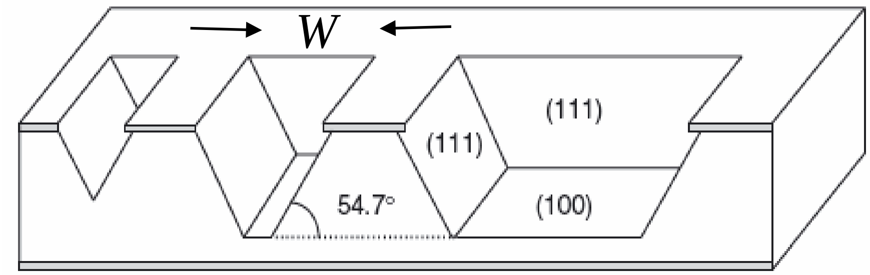


Figure 20.1 Anisotropic wet-etched profiles in <100> wafer. The sloped sidewalls are the slow etching (111) planes; the horizontal planes are (100). Etching will terminate if the slow etching (111) planes meet

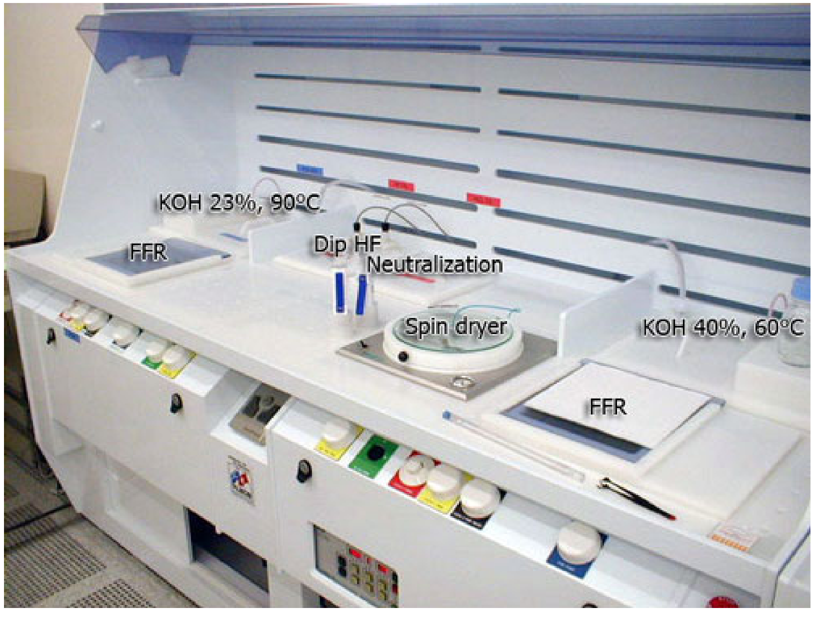
Self limiting depth: $d = \dfrac{W}{\sqrt{2}}$

KOH etches Si {110} > {100} > {111}, producing a characteristic anisotropic V-etch, with sidewalls that form a 54.7° angle with the surface (35.3° from the normal).

http://www.ece.uncc.edu/research/clean_room/fabprocesses/KOH-EtchingAndDecon.pdf

CENTER OF MICRONANOTECHNOLOGY CMI

KOH WETBENCH MANUAL



Printer friendly version (here)

Etching through a wafer can take hours

To be read first:

- SAFETY OPERATOR MANUAL (HERE) / PROCÉDURE DE SÉCURITÉ POUR OPÉRER SUR LES WETBENCH DU CMI A LIRE OBLIGATOIREMENT (ICI)
- RESIST IS TOTALLY FORBIDEN INTO THESE BATHES
- THE KOH ETCH RATE COULD VARY: FOR ACCURATE ETCHING PLEASE CALIBRAT IT BEFORE PROCESSING LIVE WAFERS

https://cmi.epfl.ch/etch/PladeKOH.php

KOH etching of silicon

The <111> planes are etched 200 times slower than <100> planes.

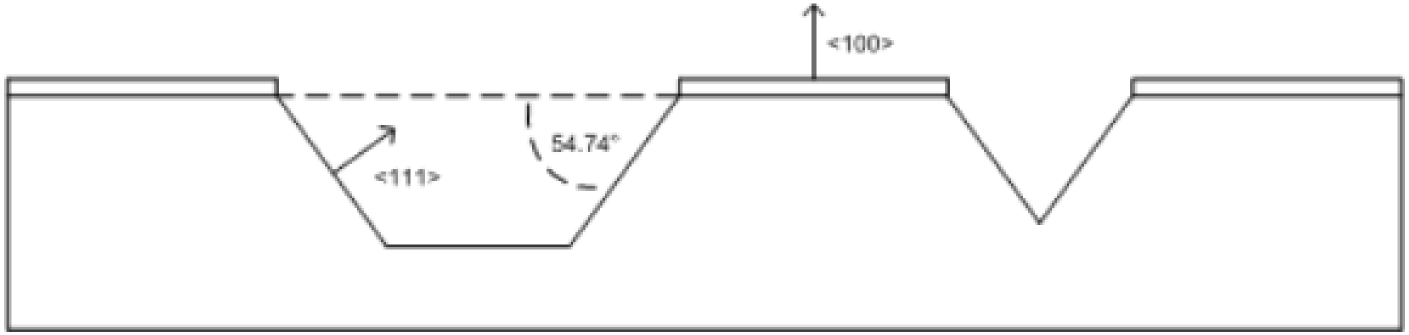


Figure 1: Typical profile obtains after Si <100> etching

T°C	Si Etch Rate (µm/h)	Selectivity Si/SiO2	Bath density
60	18.7 (±2)	290	1.38

Table 1: 40% KOH bath

T°C	Si Etch Rate (µm/h)	Selectivity Si/SiO2	Selectivity Si/Si3N4	bath density
60	25	458:1	more than 25000:1	1.20
70	42	349:1	more than 25000:1	1.20
80	74	277:1	more than 25000:1	1.21
90	120	204:1	more than 25000:1	1.22

Table 2: 23% KOH bath

https://cmi.epfl.ch/etch/PladeKOH.php

Other anisotropic etchants for silicon

Etchant	Operating temp (°C)	R_{100} (μm/min)	$S=R_{100}/R_{111}$	Mask materials
Ethylenediamine pyrocatechol (EDP)[2]	110	0.47	17	SiO_2, Si_3N_4, Au, Cr, Ag, Cu
Potassium hydroxide/Isopropyl alcohol (KOH/IPA)	50	1.0	400	Si_3N_4, SiO_2 (etches at 2.8 nm/min)
Tetramethylammonium hydroxide (TMAH)[3]	80	0.6	37	Si_3N_4, SiO_2

EDP (an aqueous solution of ethylene diamine and pyrocatechol), displays a <100>/<111> selectivity of 17X, does not etch silicon dioxide as KOH does, and also displays high selectivity between lightly doped and heavily boron-doped (p-type) silicon.

Tetramethylammonium hydroxide (TMAH) presents a safer alternative than EDP, with a 37X selectivity between {100} and {111} planes in silicon.

http://en.wikipedia.org/wiki/Etching_%28microfabrication%29

HF etching of SiO_2

$$SiO_2 + 6\ HF = 2H^+\ SiF_6^{2-} + 2H_2O$$

Stops at the silicon surface and leaves the surface hydrogen passivated.

HF is dangerous and you require special training before using it. Larger labs have a dedicated HF station.

HF reacts with glass, concrete, metals, water, oxidizers, reducers, alkalis, combustibles, organics and ceramics. It must be kept in special polyethylene or fluorocarbon plastic containers and special tools are used.

Etch-stop techniques

p+ etch stop

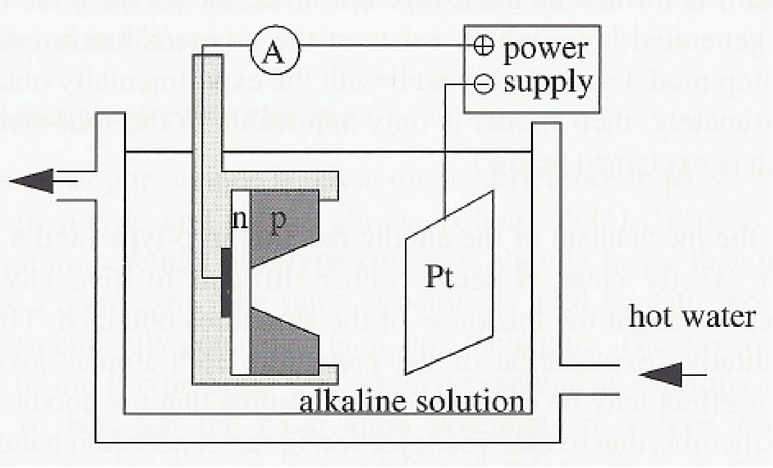
silicon highly doped (>10^{19} cm^{-3}) with boron etches very slowly

Etch stop with buried masking layers

implant O, N, or C to make SiO_2, SiC, or SiN_x

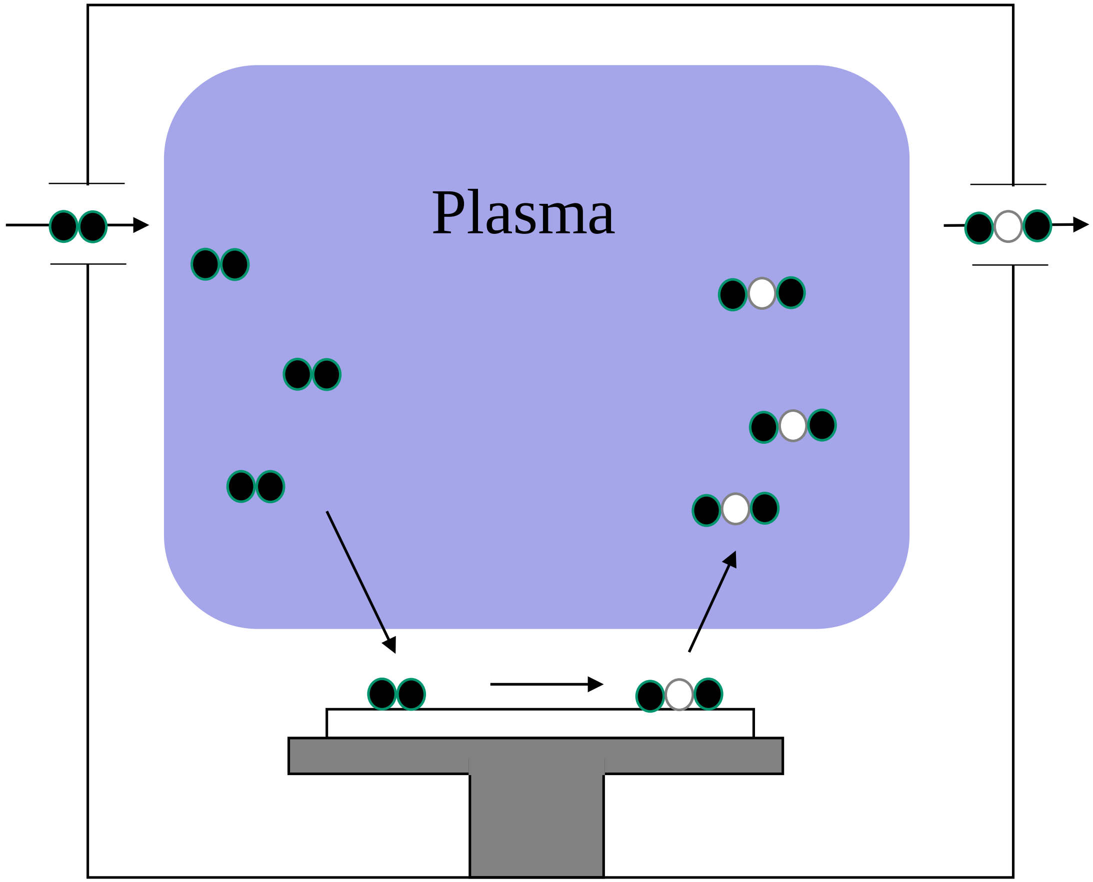
Electrochemically controlled pn etch stop

The voltage drops across the reverse biased junction until the n region is exposed and then the potential drop at the surface oxidizes the silicon and stops the etching.



http://memslibrary.com/guest-articles/47-silicon-etching/4-etch-stop-techniques-for-etching-of-silicon-in-alkaline-solutions.html

Plasma etching



The plasma activates the etching gas which reacts at the surface to form a gaseous product.

(In PECVD a solid product is formed.)

http://en.wikipedia.org/wiki/Etching_%28microfabrication%29

Etchants for common microfabrication materials

Material to be etched	Wet etchants	Plasma etchants
Aluminium (Al)	80% phosphoric acid (H_3PO_4) + 5% acetic acid + 5% nitric acid (HNO_3) + 10% water (H_2O) at 35–45 °C[4]	Cl_2, CCl_4, $SiCl_4$, BCl_3[5]
Indium tin oxide [ITO] (In_2O_3:SnO_2)	Hydrochloric acid (HCl) + nitric acid (HNO_3) + water (H_2O) (1:0.1:1) at 40 °C[6]	
Chromium (Cr)	• "Chrome etch": ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$) + nitric acid (HNO_3)[7] • Hydrochloric acid (HCl)[7]	
Gallium Arsenide (GaAs)	• Citric Acid diluted ($C_6H_8O_7$: H_2O, 1 : 1) + Hydrogen Peroxide (H_2O_2)+ Water (H_2O)	• Cl_2, CCl_4, $SiCl_4$, BCl_3, CCl_2F_2
Gold (Au)	Aqua regia, Iodine and Potassium Iodide solution	
Molybdenum (Mo)		CF_4[5]
Organic residues and photoresist	Piranha etch: sulfuric acid (H_2SO_4) + hydrogen peroxide (H_2O_2)	O_2 (ashing)
Platinum (Pt)	Aqua regia	
Silicon (Si)	• Nitric acid (HNO_3) + hydrofluoric acid (HF)[4] • Potassium hydroxide (KOH) • Ethylenediamine pyrocatechol (EDP) • Tetramethylammonium hydroxide (TMAH)	• CF_4, SF_6, NF_3[5] • Cl_2, CCl_2F_2[5]
Silicon dioxide (SiO_2)	• Hydrofluoric acid (HF)[4] • Buffered oxide etch [BOE]: ammonium fluoride (NH_4F) and hydrofluoric acid (HF)[4]	CF_4, SF_6, NF_3[5]
Silicon nitride (Si_3N_4)	• 85% Phosphoric acid (H_3PO_4) at 180 °C[4] (Requires SiO_2 etch mask)	CF_4, SF_6, NF_3,[5] CHF_3
Tantalum (Ta)		CF_4[5]
Titanium (Ti)	Hydrofluoric acid (HF)[4]	BCl_3[8]
Titanium nitride (TiN)	• Nitric acid (HNO_3) + hydrofluoric acid (HF) • SC1 • Buffered HF (bHF)	

Plasma etching

The same equipment can be used for

- plasma etching
- plasma cleaning
- surface modification

Leaves less residue than wet etching. The products are volatile.

Ion Milling

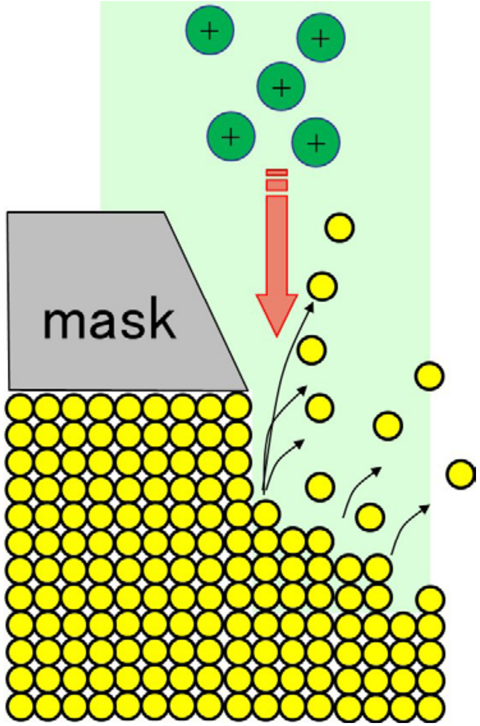
Ions (typically Ar) are accelerated at the substrate.

No chemical reaction

Selectivity ~ 1:1

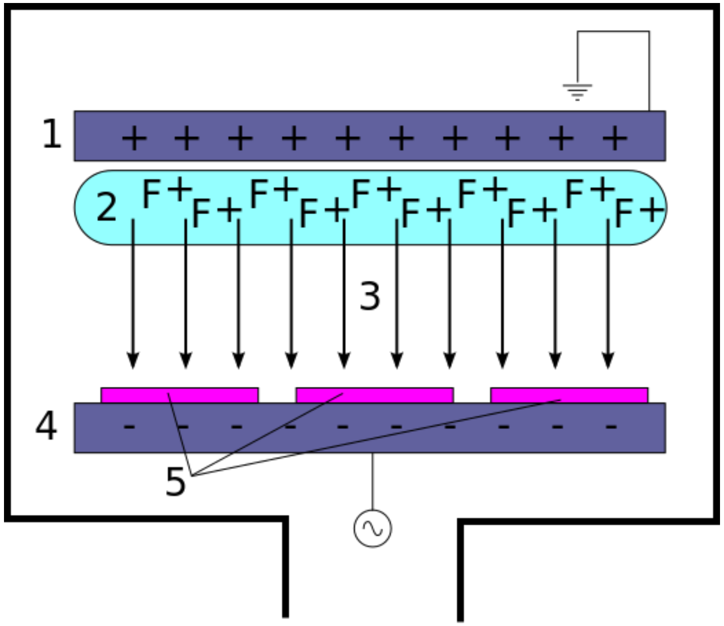
High vacuum

Will etch anything



http://hitachi-hta.com/products/electron-ion-and-probe-microscopy/ion-beam-milling/im4000-ion-milling-system

Reactive Ion Etching (RIE)



http://en.wikipedia.org/wiki/Reactive-ion_etching

Combines physical ion milling with chemical etching.
Is faster and more selective than ion milling.

Isotropic and Anisotropic Plasma Etching

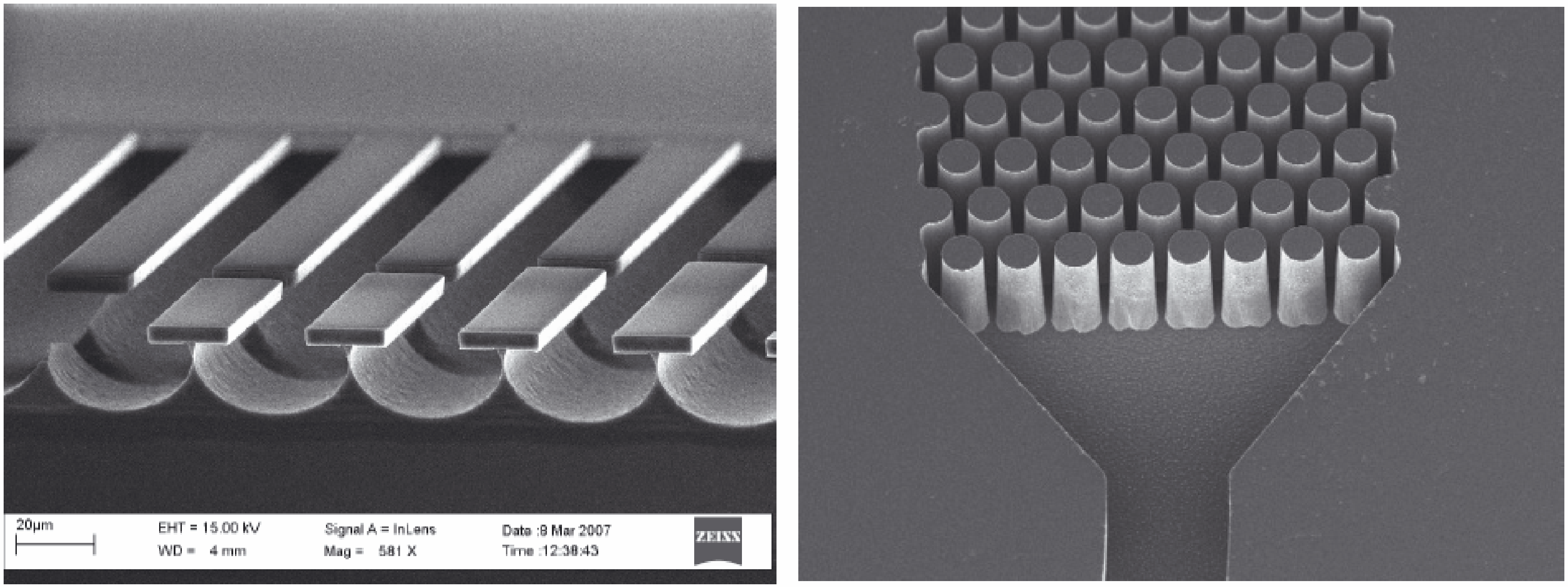


Figure 11.4 Isotropic (left) and anisotropic etch profiles (right)

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You can use plasma etching to etch isotropically and anistotropically.

Isotropic and Anisotropic Plasma Etching

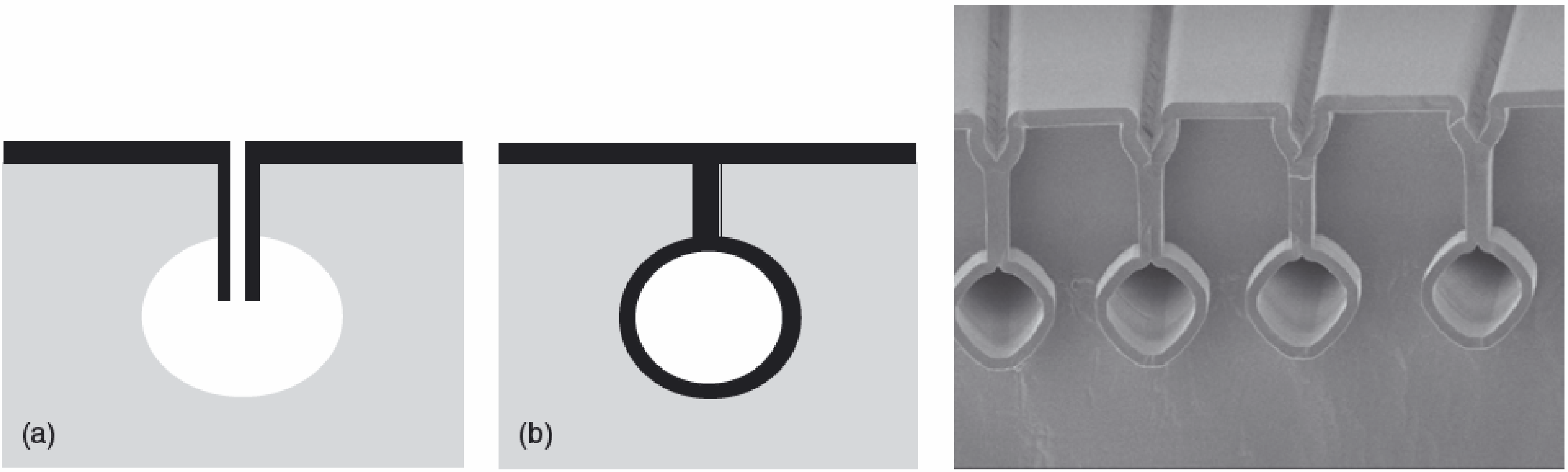

Figure 21.15 Buried microchannels: (a) anisotropic DRIE, sidewall spacer formation and isotropic DRIE; (b) removal of spacer and conformal CVD. SEM micrograph from de Boer *et al*. (2000) by permission of IEEE

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Channels used for microneedles.

Microbolometer

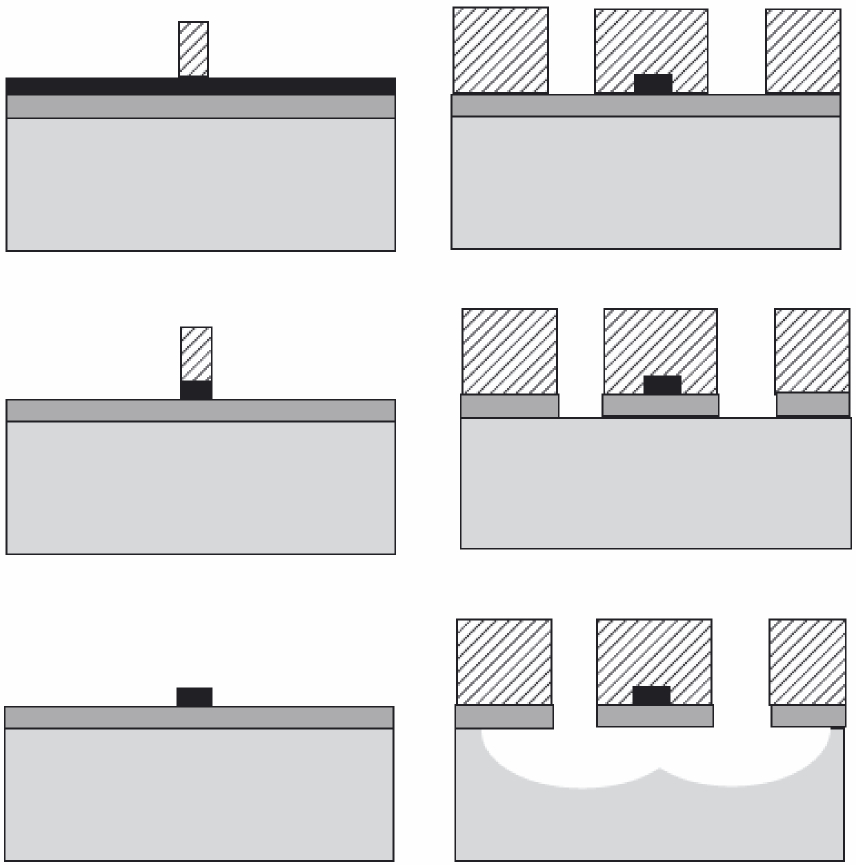

Figure 11.15 Bolometer fabrication process: left, resistor lithography and etching; right, second lithography, oxide etching and silicon isotropic etching

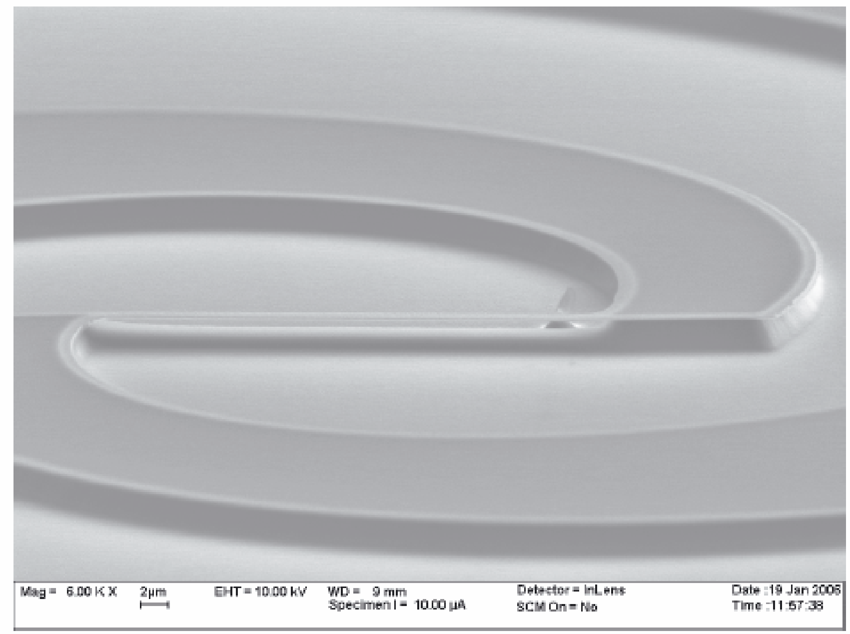

Figure 11.16 Spiral antenna microbolometer: silicon is isotropically etched to release the narrow resistor. SEM courtesy Leif Grönberg, VTT

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Bosch process

Repeat 2 processes over and over

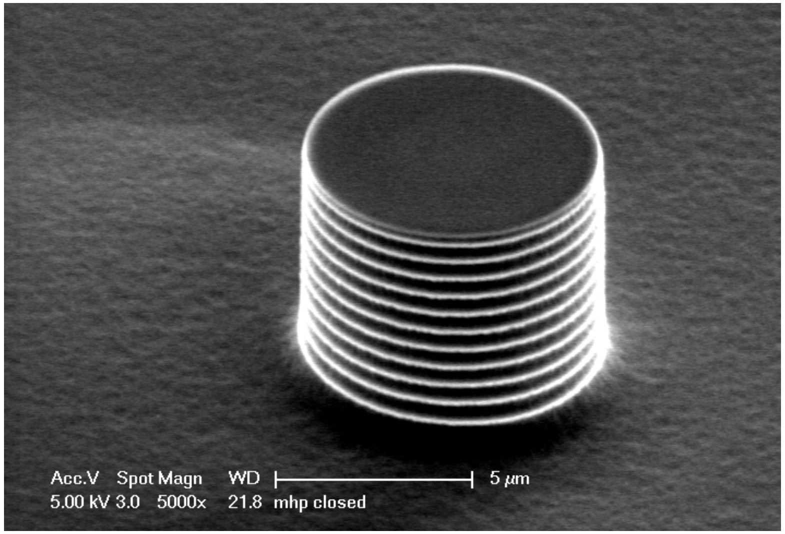
1. Etch Si with SF_6 (nearly isotropic)

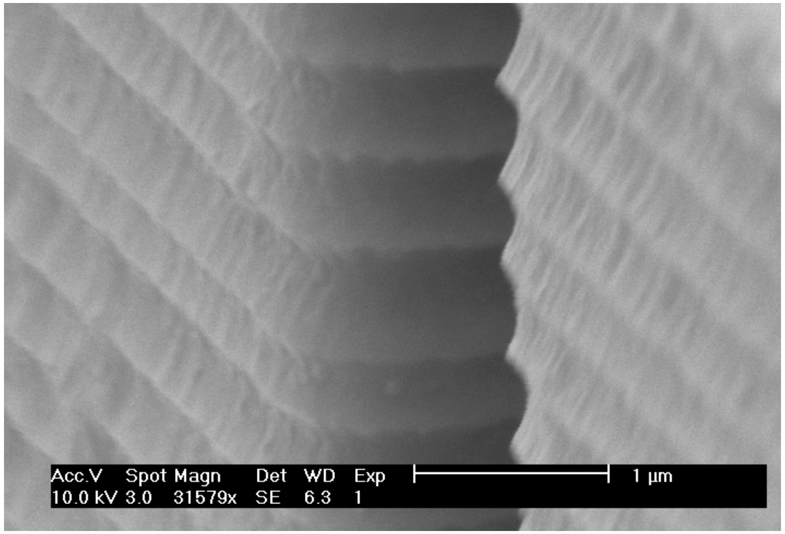
2. Deposit passivation layer C_4F_8

Directional etching at the bottom breaks through the passivation layer.

Short cycles: smooth walls

Long cycles: fast etching

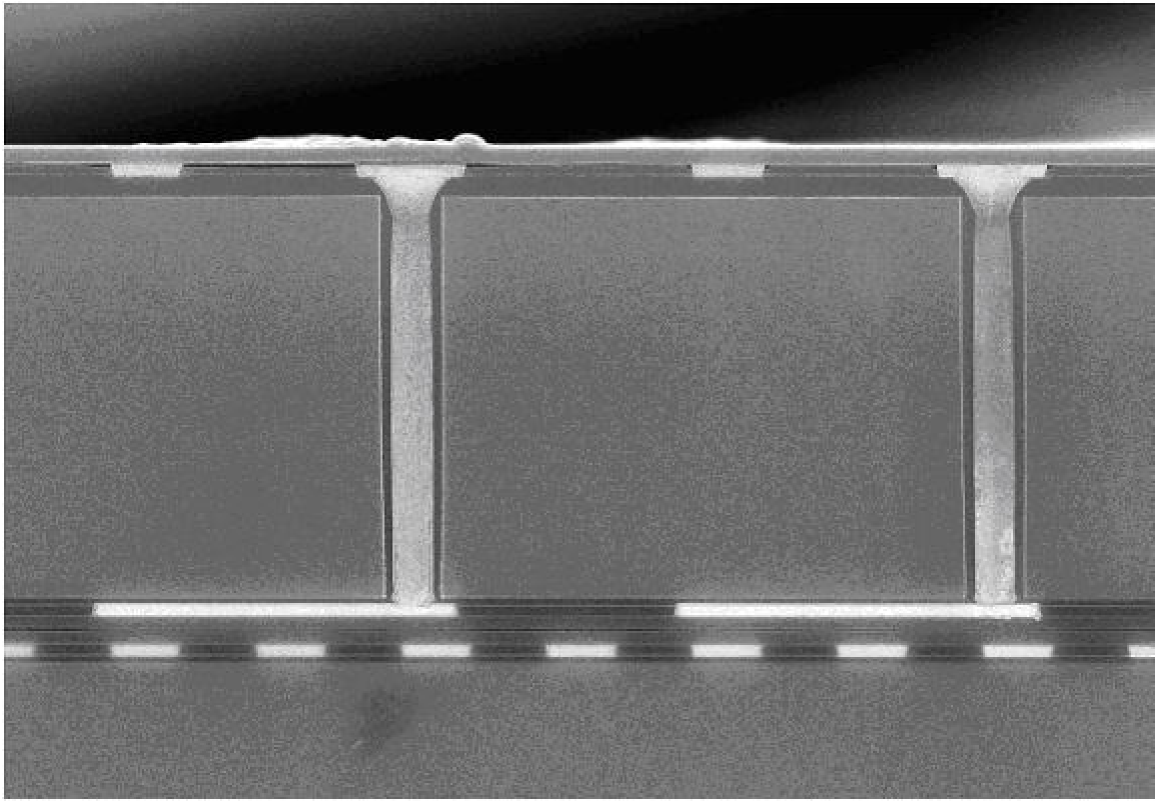




http://en.wikipedia.org/wiki/Deep_reactive-ion_etching

Through-Silicon Via (TSV)

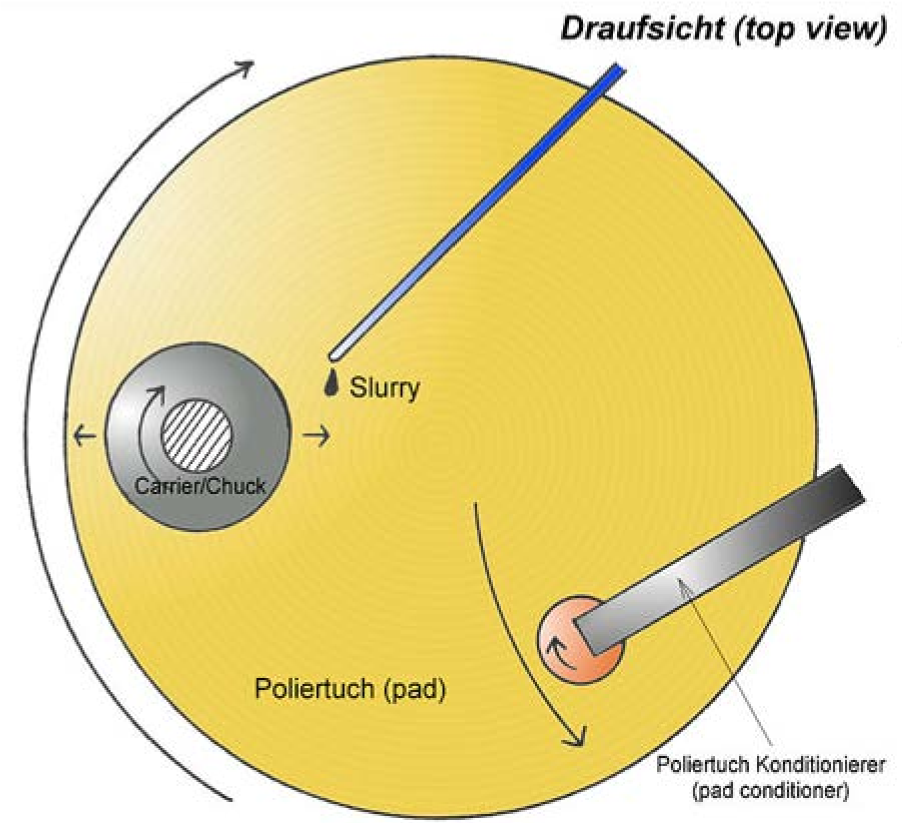
http://javier.esilicon.com/2011/01/30/thru-silicon-vias-current-state-of-the-technology/

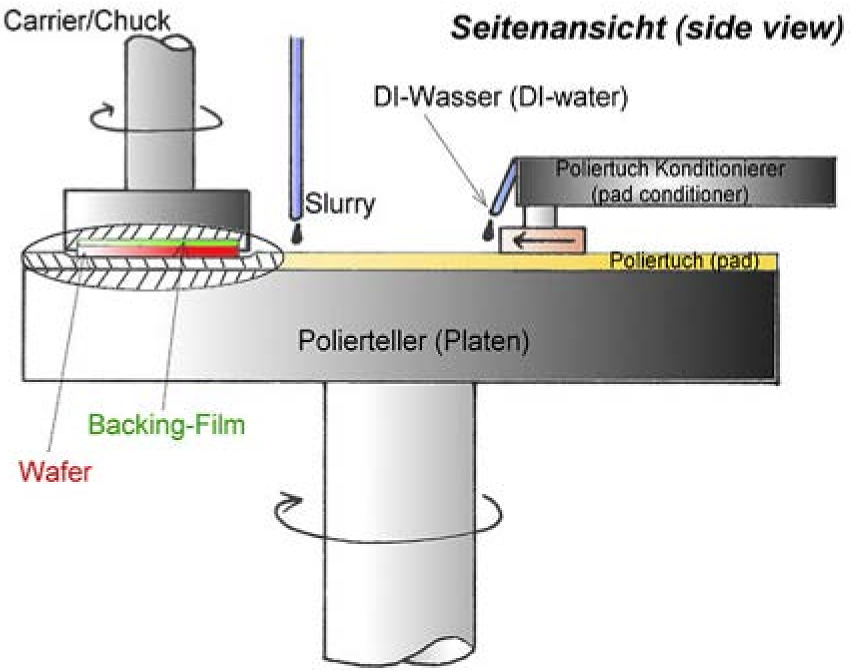


A vertical electrical connection (via) passing completely through a silicon wafer.

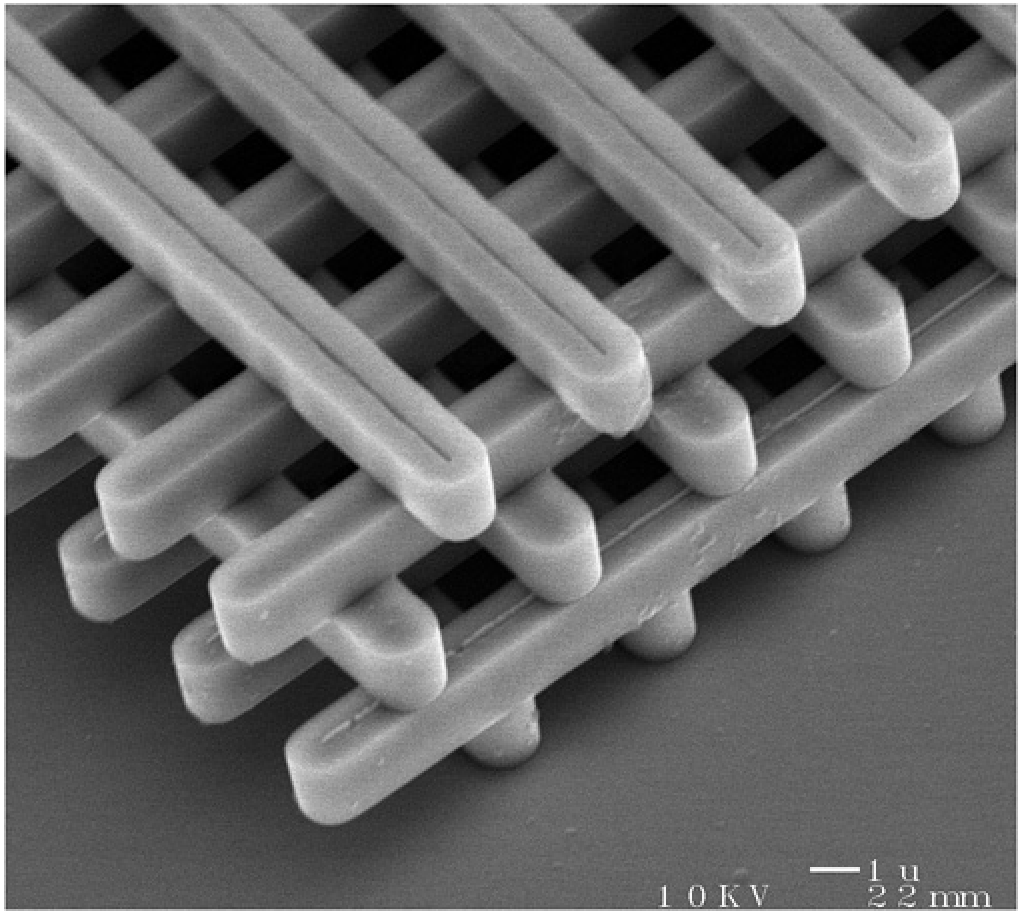
Used in 3D integration.

Chemical Mechanical Polishing (CMP)





Woodpile photonic crystal



http://www.sandia.gov/media/photonic.htm

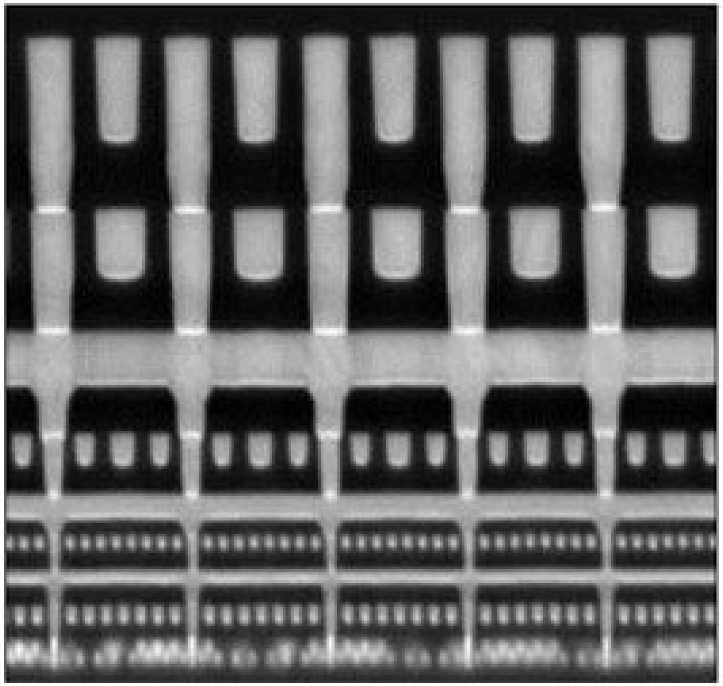
Damascene process

Inlaying of one metal in another

http://en.wikipedia.org/wiki/Damascening#/media/File:Damascening.jpg

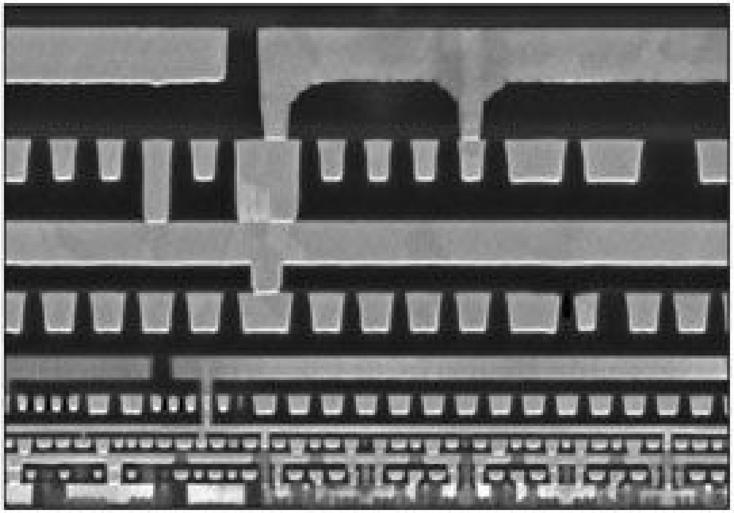
Interconnects

22 nm Process



80 nm minimum pitch

14 nm Process



52 nm (0.65x) minimum pitch

http://www.tomshardware.com/reviews/intel-14nm-broadwell-y-core-m,3904.html

Cleaning

Wafer cleaning is about 30% of all processes.

Particles - brushes, water jets, shockwaves
cause: lithography defects, pinholes, shorts
Organics - peroxide, O_2 plasma
hydrophobic (inhibits water cleaning)
residues keep subsequent layers from sticking
Metals - Acids ($HCl–H_2O_2$ and $H_2SO_4–H_2O_2$)
Oxide - HF

Clean rooms

Filtered air to remove particles
Overpressure maintained to blow dirt out
Controlled temperature and humidity
    Important to make processes reproducible

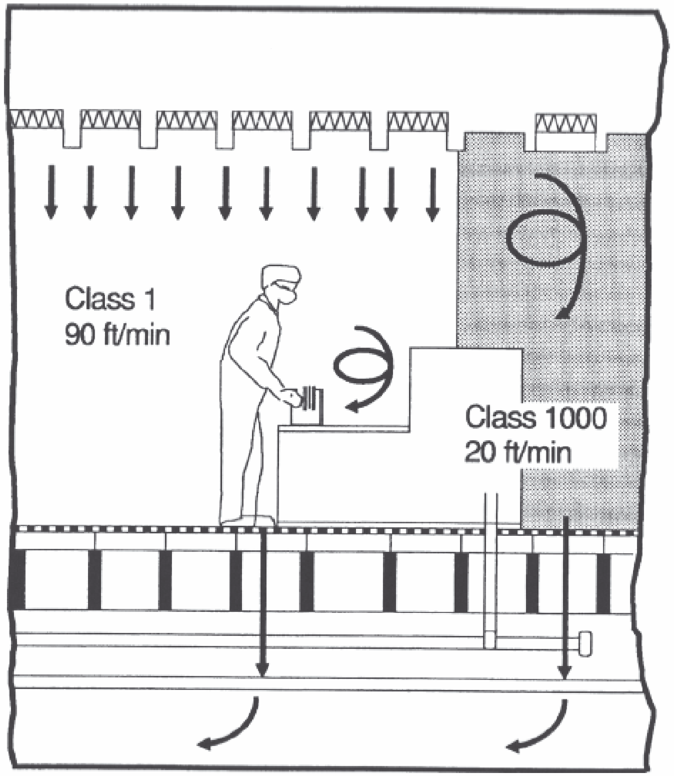


Figure 35.5 Cleanroom and gray area: ISO 3 (Class 1) area for wafer processing, ISO 6 (Class 1000) turbulent flow in service aisle Reproduced from Whyte (2001) by permission of John Wiley & Sons, Ltd

http://www.cleanroominnovation.com

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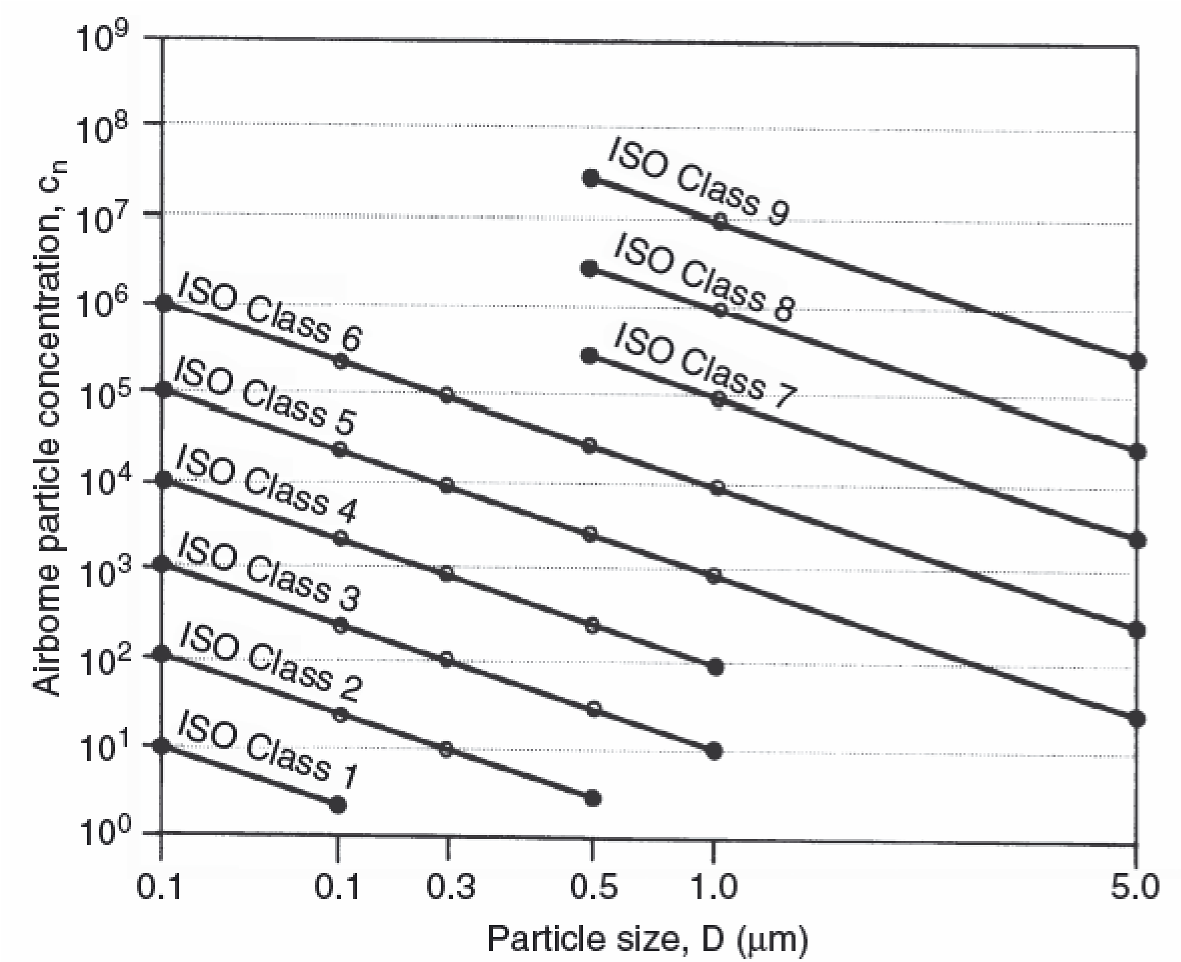
Particles

Flakes from chamber walls
Wear of mechanical parts



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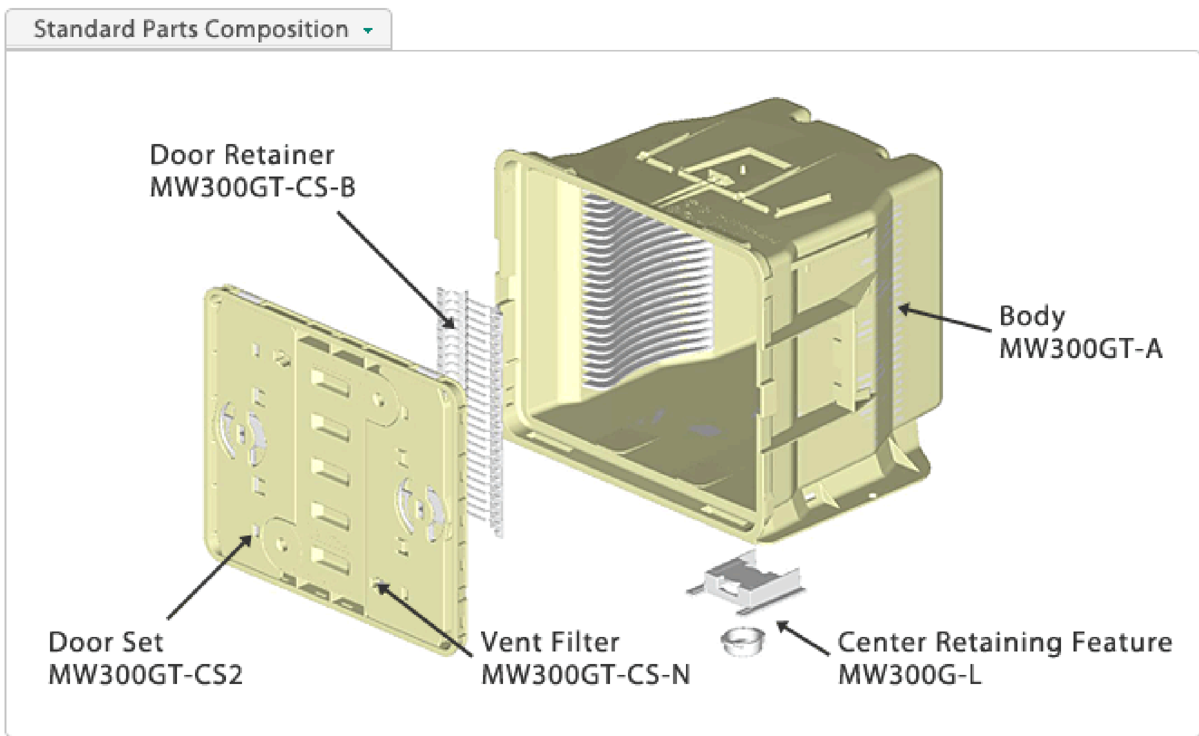
The concentration of particles increases exponentially as their size decreases.

Foup (Front Opening Universal Pod)

- FIMS Door/Automated operation
- Manual open/close function
- Robust structure for perfect seal during transportation
- Design to minimize Cleaning and Drying Cycle Time
- Conforms to SEMI Standard M31

Dimensions	:	W389 x L340 x H331 (mm)
Weight	:	7.5kg(16.9lb) Including 25 wafers
		4.3kg(9.7lb) without wafers



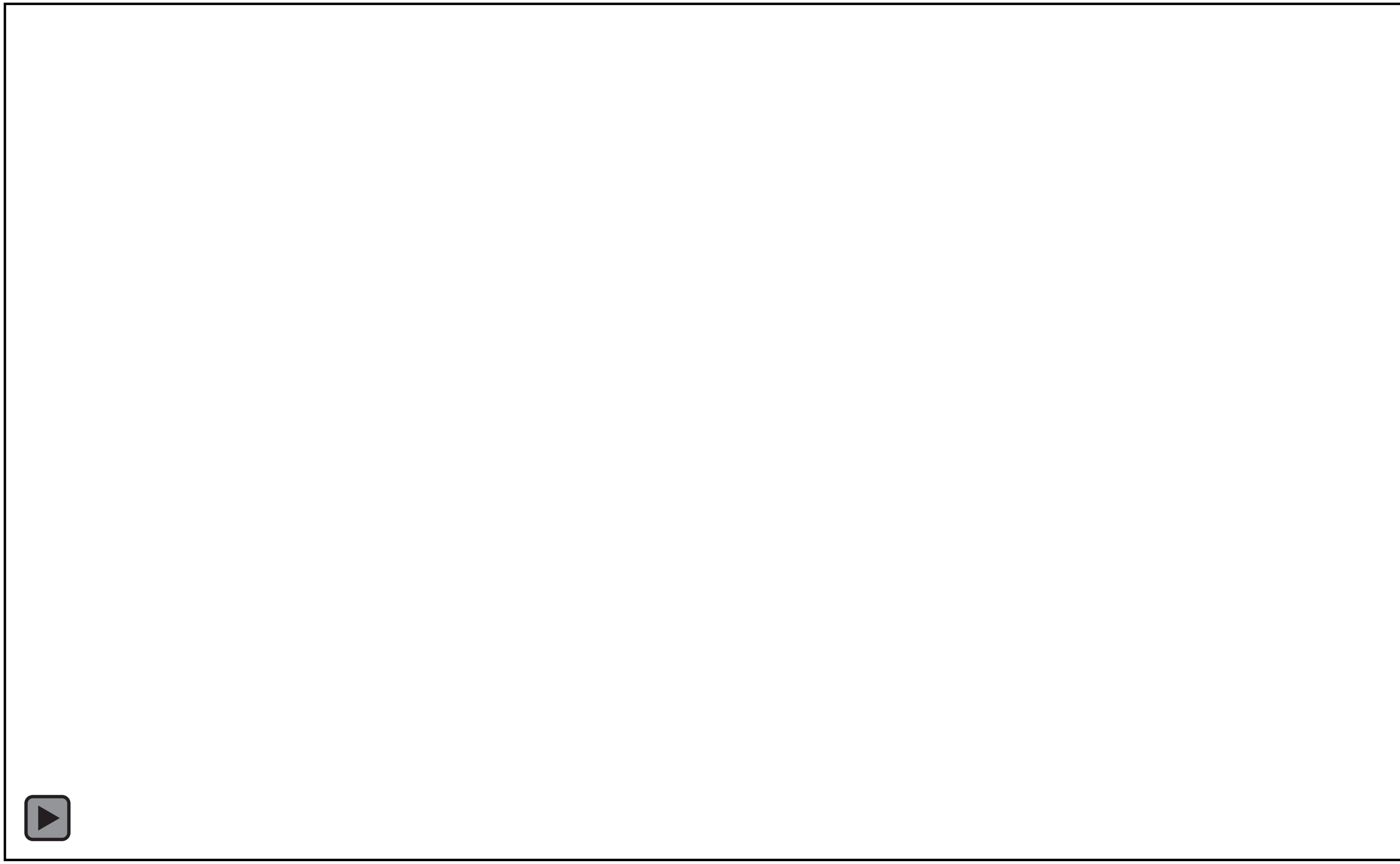
https://www.shinpoly.co.jp/business/seimitsu/300gt/index.html

Wafer handling

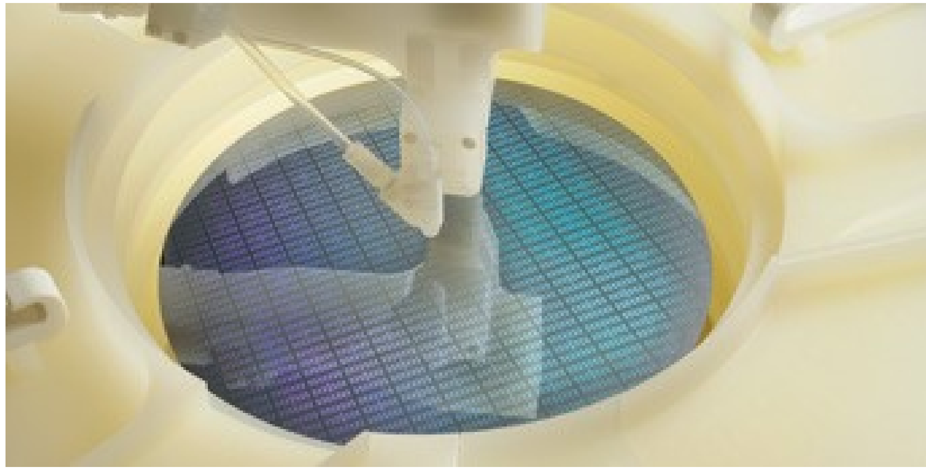
Wafer transport

https://www.youtube.com/watch?v=-KTKg0Y1snQ

Foup cleaning



Cleaning



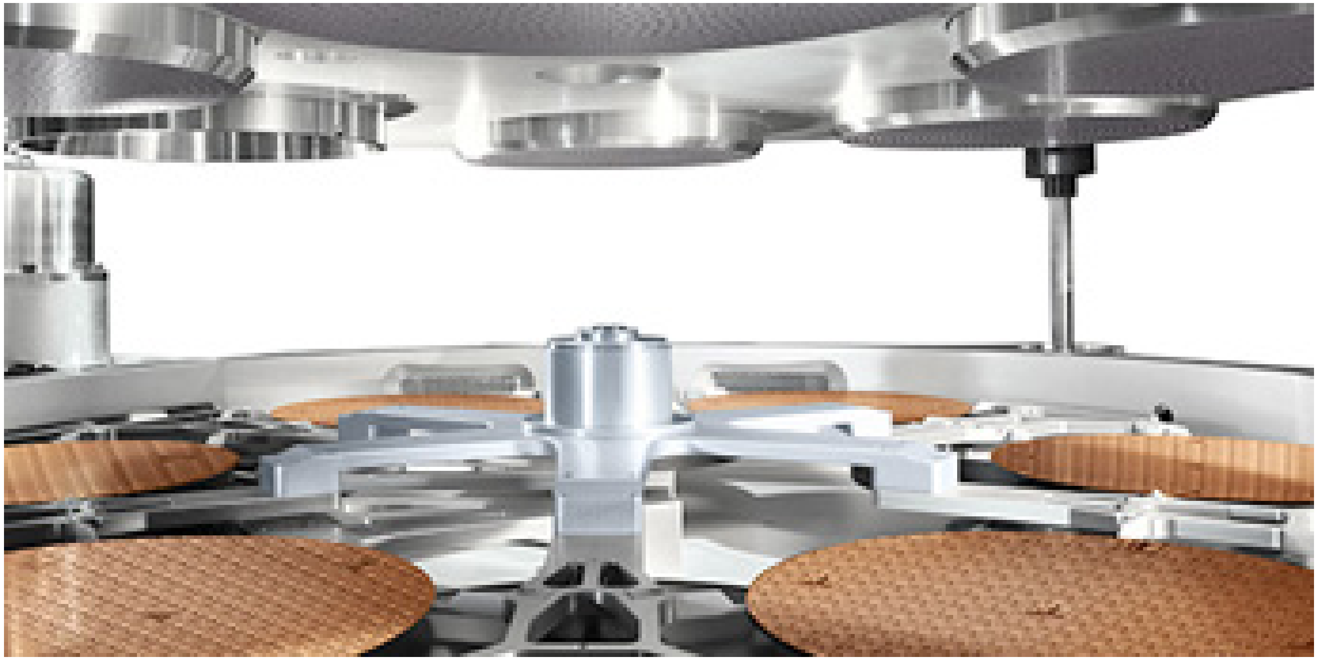
Wafer cleaning is a critical function that must be repeated many times during semiconductor manufacturing.

KEY APPLICATIONS

- Particle, polymer, and residue removal
- Photoresist removal
- Backside/bevel cleaning and film removal

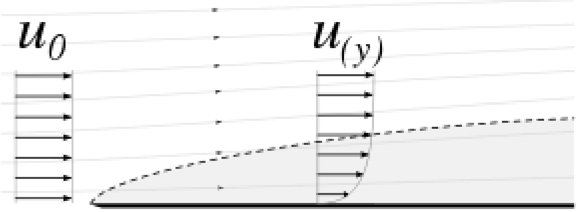
Villach/Austria is the global centre for the development and production of all single-wafer spin technology products for back- and front- end-of-line (BEOL/FEOL) cleaning, etching and stripping applications.

Photoresist strip



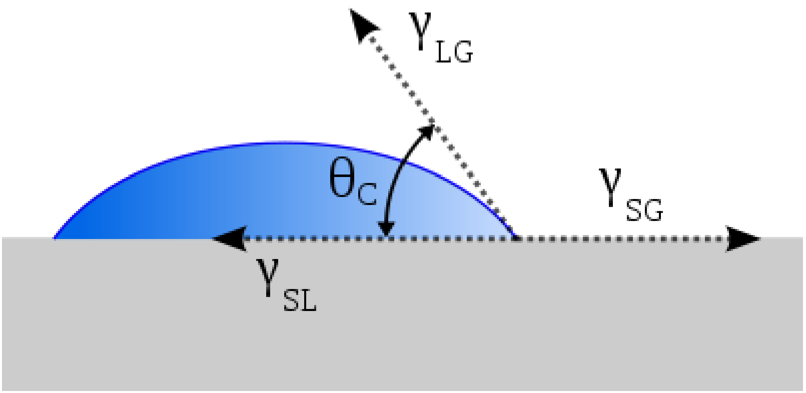
Strip processes remove photoresist material after it has served to "protect" certain areas of the wafer surface from being altered.

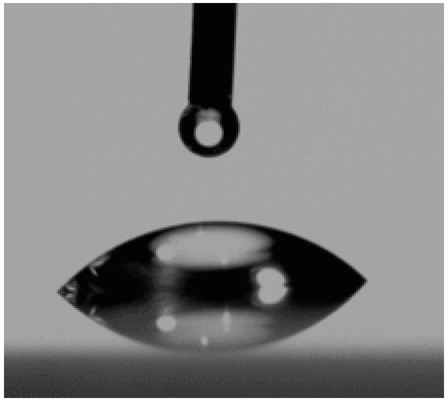
Chemistry and fluid mechanics are important.



http://www.lamresearch.com/products/strip-clean-products

Contact angle





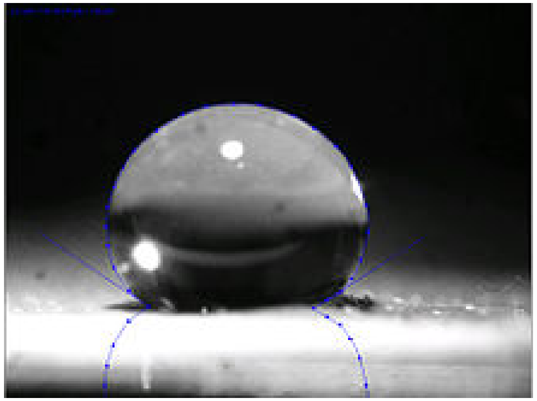


Table 12.6 Water contact angles for various surfaces and treatments

Ammonia/peroxide cleaned silicon	5°
Oxygen plasma treated SU-8	5°–40°
Sulfuric acid cleaned silicon	10°
RCA-1 + RCA-2 cleaned silicon	10°
KOH etched silicon	25°
Thermal oxide	45°
Native oxide	45°
Oxygen plasma treated PDMS	50°
HMDS coated silicon	60°
HF dipped silicon	70°
Polyimide	75°
Native SU-8	80°
Native polystyrene	90°
Native PDMS	108°
ECT (eicosanethiol)	110°
Fluoropolymer	120°
Microstructure + PDMS	150°
Nanostructure + fluoropolymer	170°

Note that all the values are approximate and depend on surface treatment details and duration, and on time delay.

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

Dry cleaning

Etching using plasmas or gases
Can be used in a MBE or CVD chamber
Ozone/UV for organics
HF vapors for oxide
Cl_2 for metals
Ar milling/sputter cleaning for anything

Drying

DI water -> IPA -> Blow dry N_2