

微纳光电子材料与器件工艺原理

Cleanroom Environment and Wafer Clean

Xing Sheng 盛兴

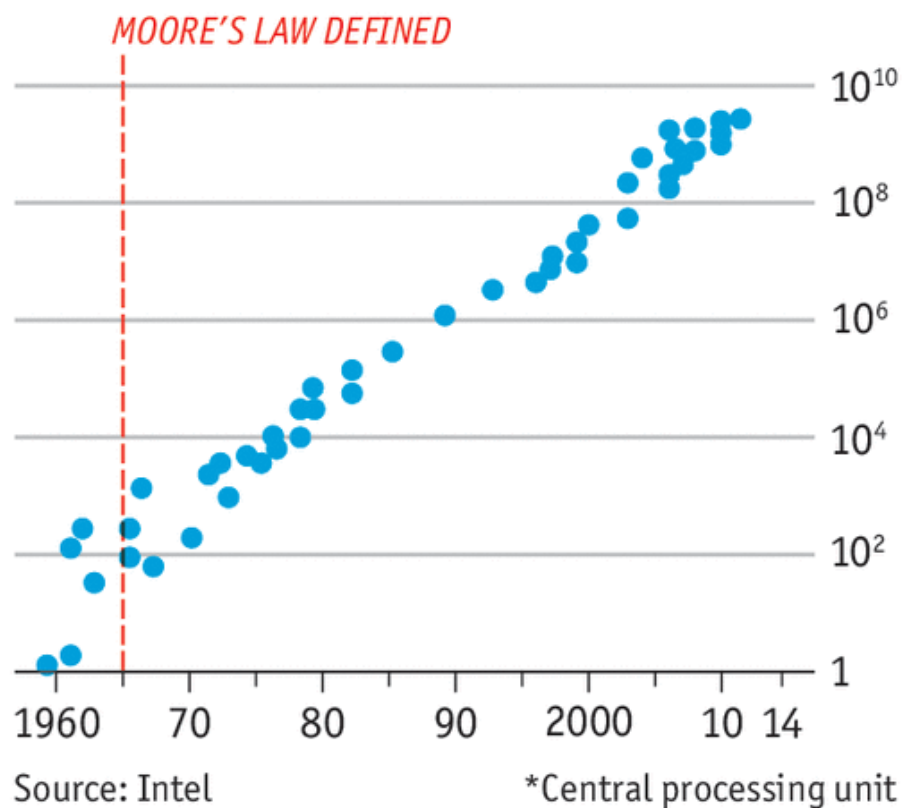


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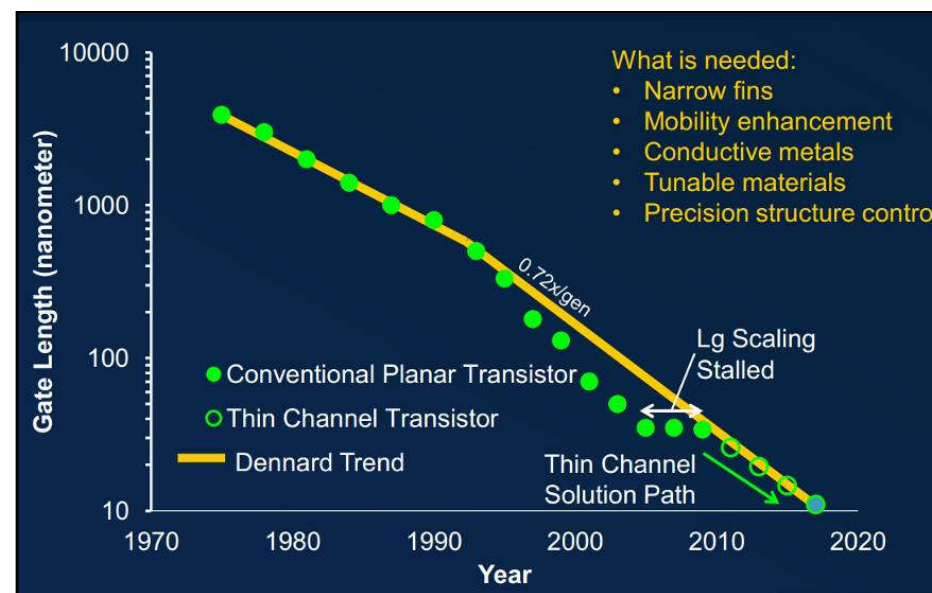
Integrate Circuits

■ Moore's law



Economist.com

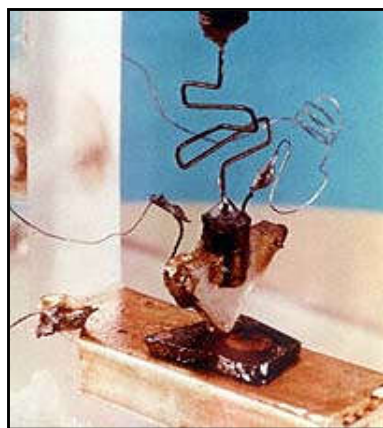
transistor number



transistor size

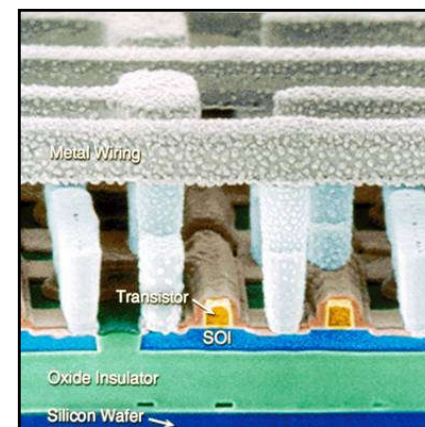
Factory Evolution

1947

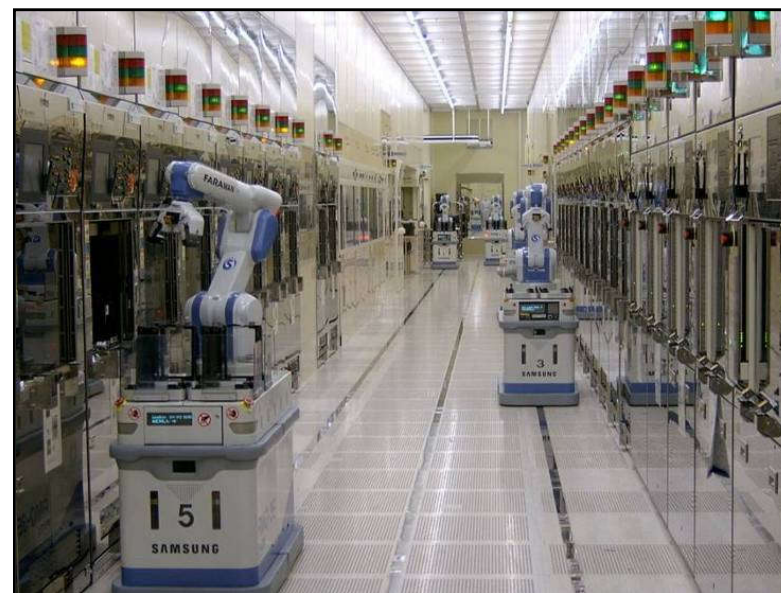


1 cm

today



< 100 nm



Factory Evolution

■ cost of new fab

- 1967 2 million \$
- 2010 10 billion \$

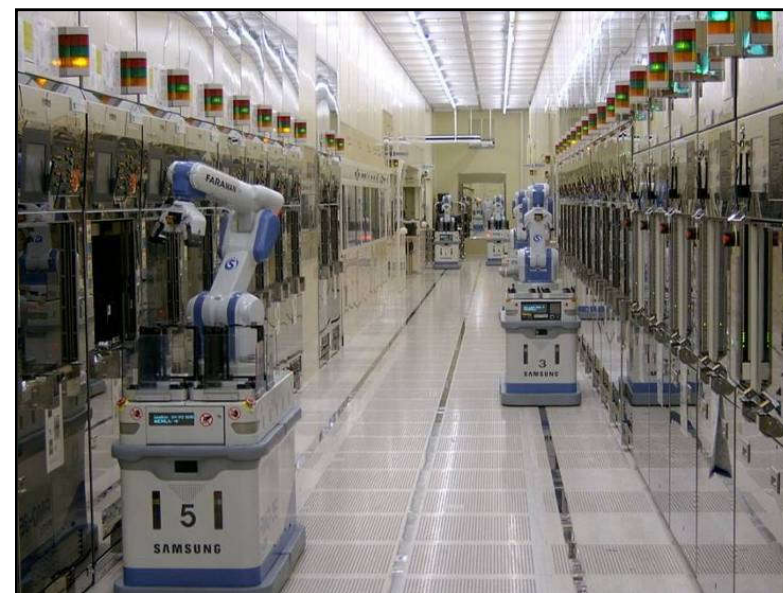
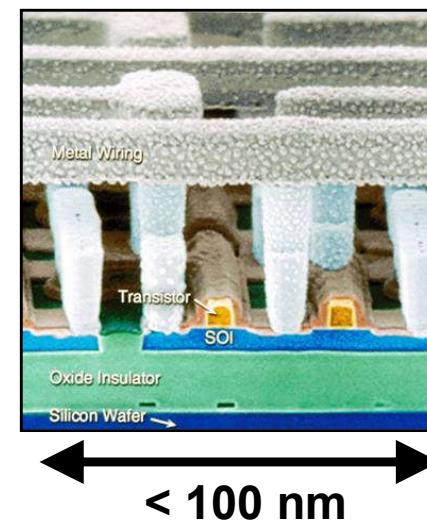
Video TSMC



武汉新芯集成电路制造有限公司 厂区鸟瞰图

2016 武汉新芯
24 billion \$\$

today



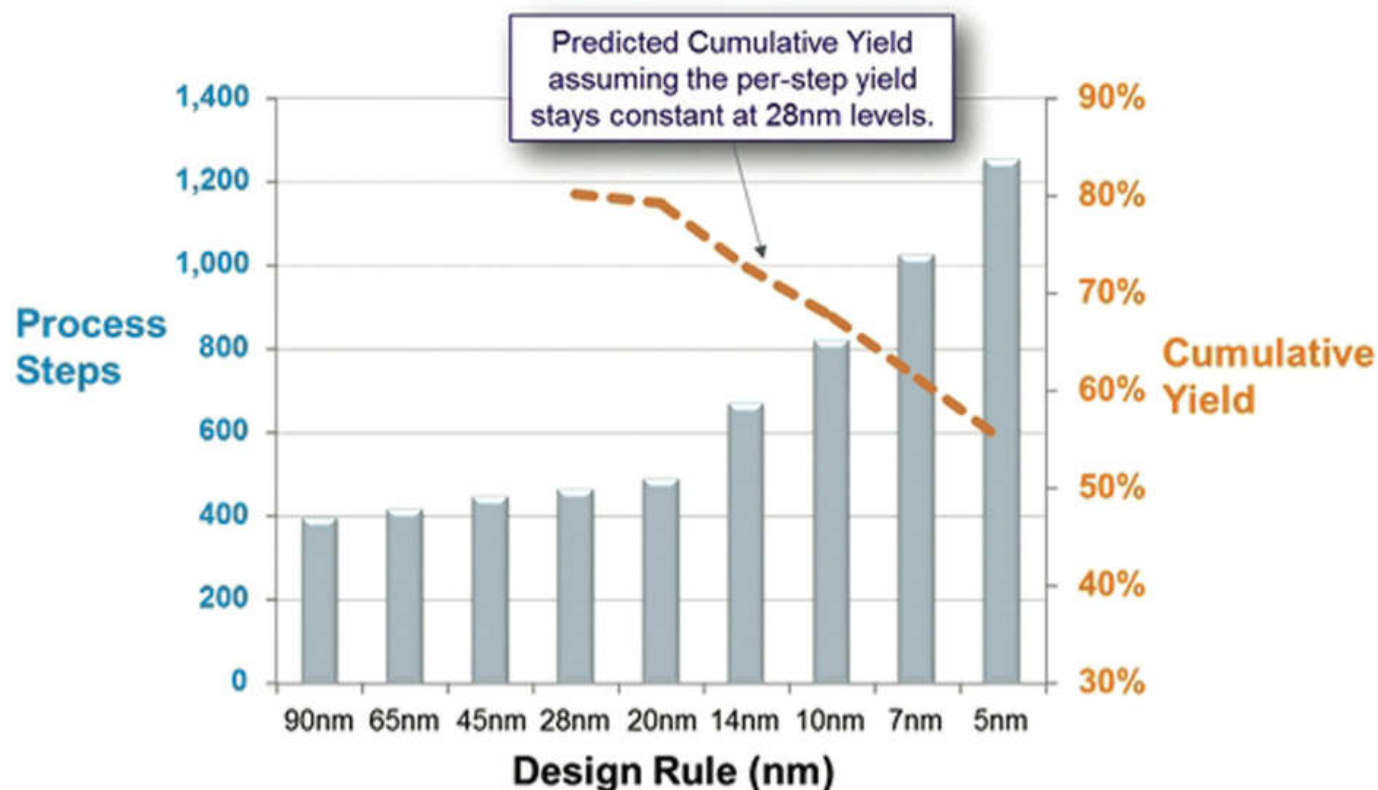
Manufacturing Yield

- Yield: rate of success

assume yield = 99% per step:

$$0.99^4 = 0.96$$

$$0.99^{400} = 0.02$$



every 1% yield increase = \$\$\$

Defects Control

environment ← **cleanroom control**

← **surface clean**

Si wafer ← **gettering**

Cleanroom Orientation

Video 1



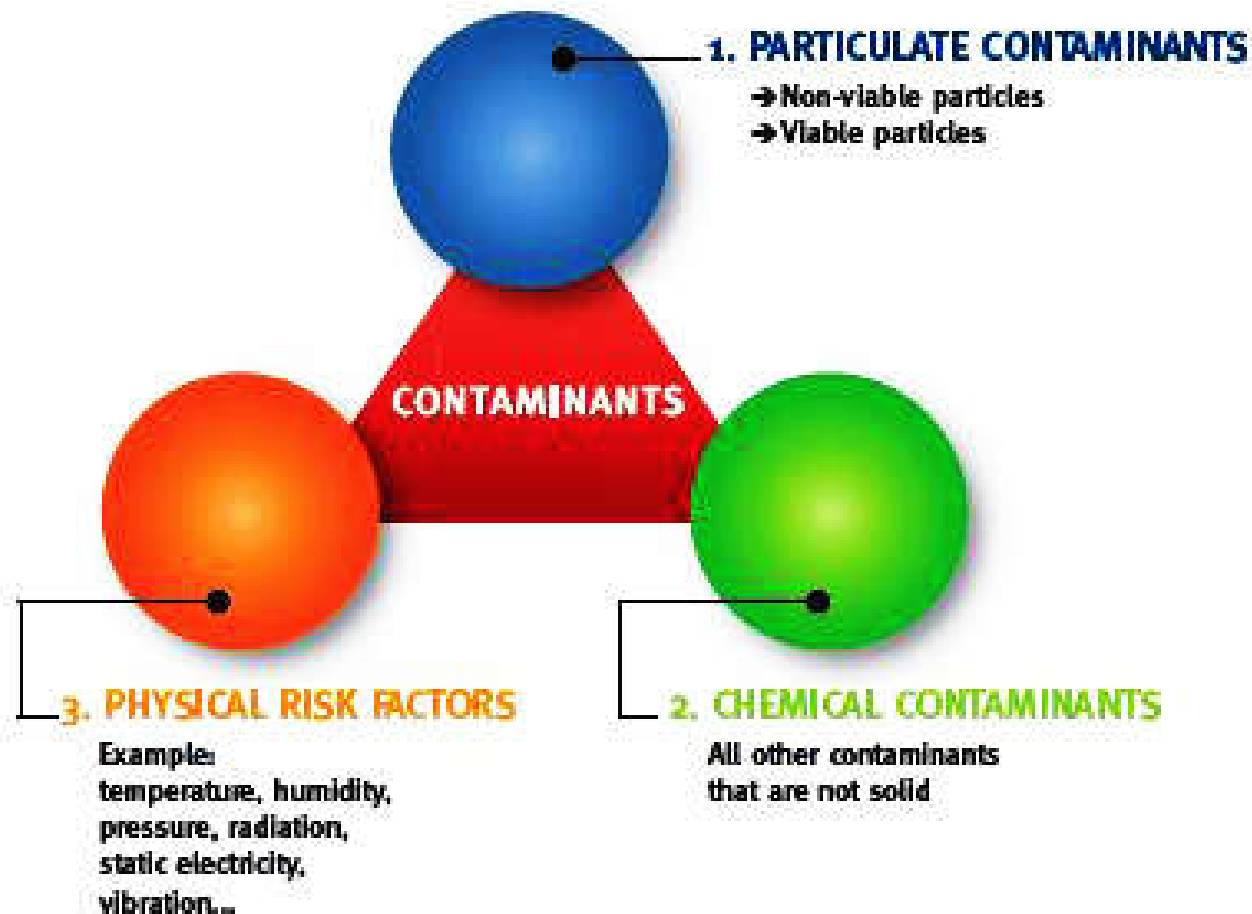
Video 2



always gown up!

Contaminations

TYPES OF CONTAMINANTS



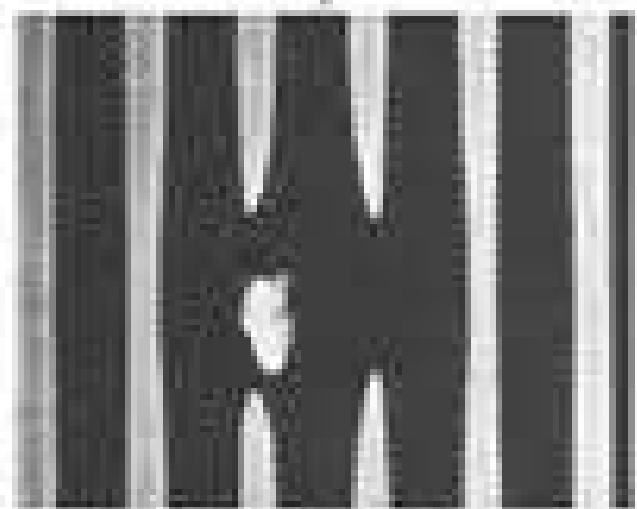
particles:

- hair
- pollen
- bacteria
- PM2.5
- ...

chemicals:

- organics
- Cu, Au
- Na, K
- ...

Particles



Open circuit

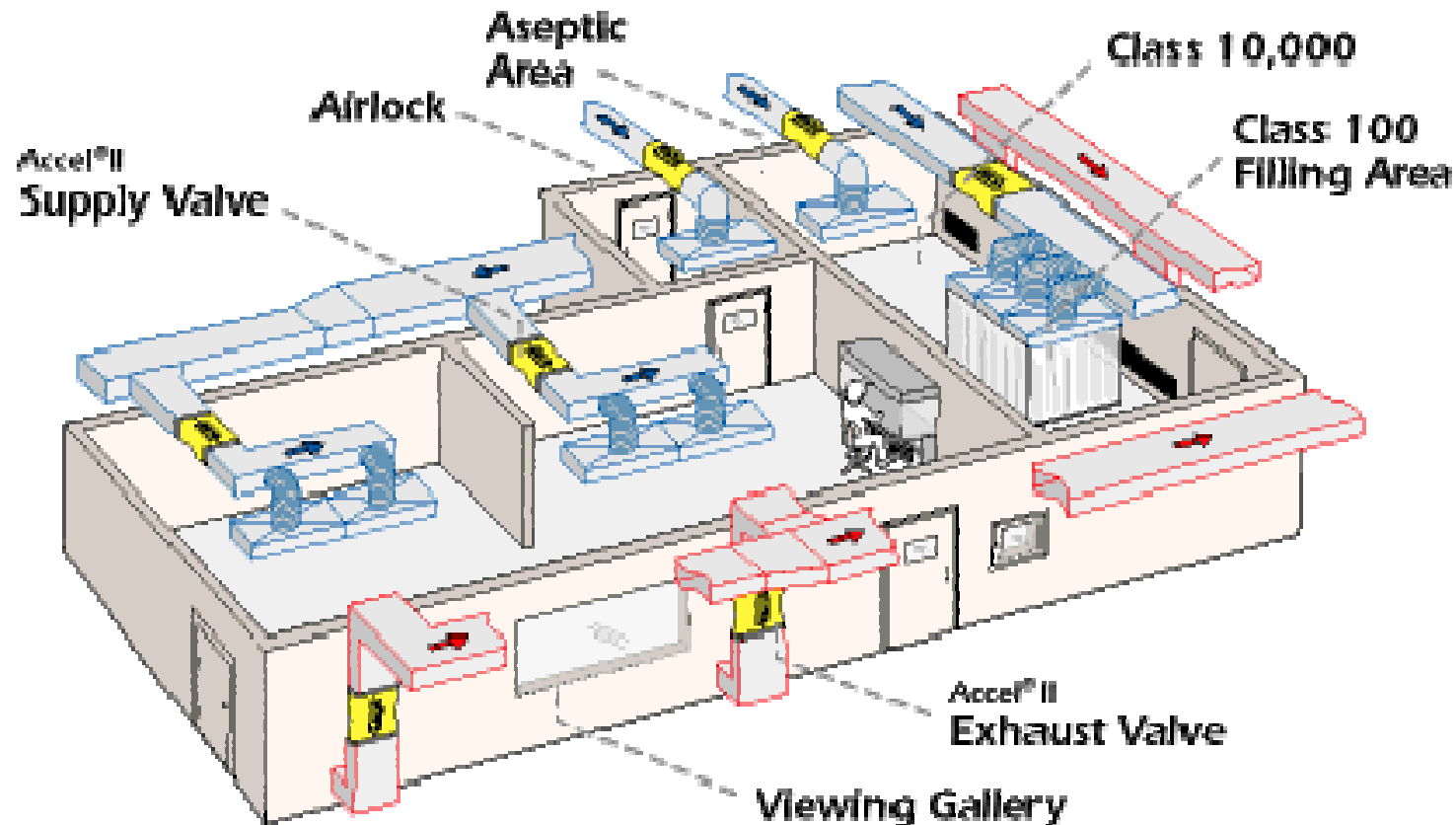


Short circuit

IC Roadmap

Year of 1st DRAM Shipment	1997	1999	2003	2006	2009	2012
Minimum Feature Size	250nm	180nm	130nm	100nm	70nm	50nm
Wafer Diameter (mm)	200	300	300	300	450	450
DRAM Bits/Chip	256M	1G	4G	16G	64G	256G
DRAM Chip Size (mm ²)	280	400	560	790	1120	1580
Microprocessor Transistors/chip	11M	21M	76M	200M	520M	1.40B
Critical Defect Size	125nm	90nm	65nm	50nm	35nm	25nm
Starting Wafer Total LLS (cm⁻²)	0.60	0.29	0.14	0.06	0.03	0.015
DRAM GOI Defect Density (cm⁻²)	0.06	0.03	0.014	0.006	0.003	0.001
Logic GOI Defect Density (cm⁻²)	0.15	0.15	0.08	0.05	0.04	0.03
Starting Wafer Total Bulk Fe (cm⁻³)	3x10¹⁰	1x10¹⁰	Under 1x10¹⁰	Under 1x10¹⁰	Under 1x10¹⁰	Under 1x10¹⁰
Metals on Wafer Surface After Cleaning (cm⁻²)	5x10⁹	4x10⁹	2x10⁹	1x10⁹	< 10⁹	< 10⁹
Starting Material Recombination Lifetime (μsec)	≥ 300	≥ 325	≥ 325	≥ 325	≥ 450	≥ 450

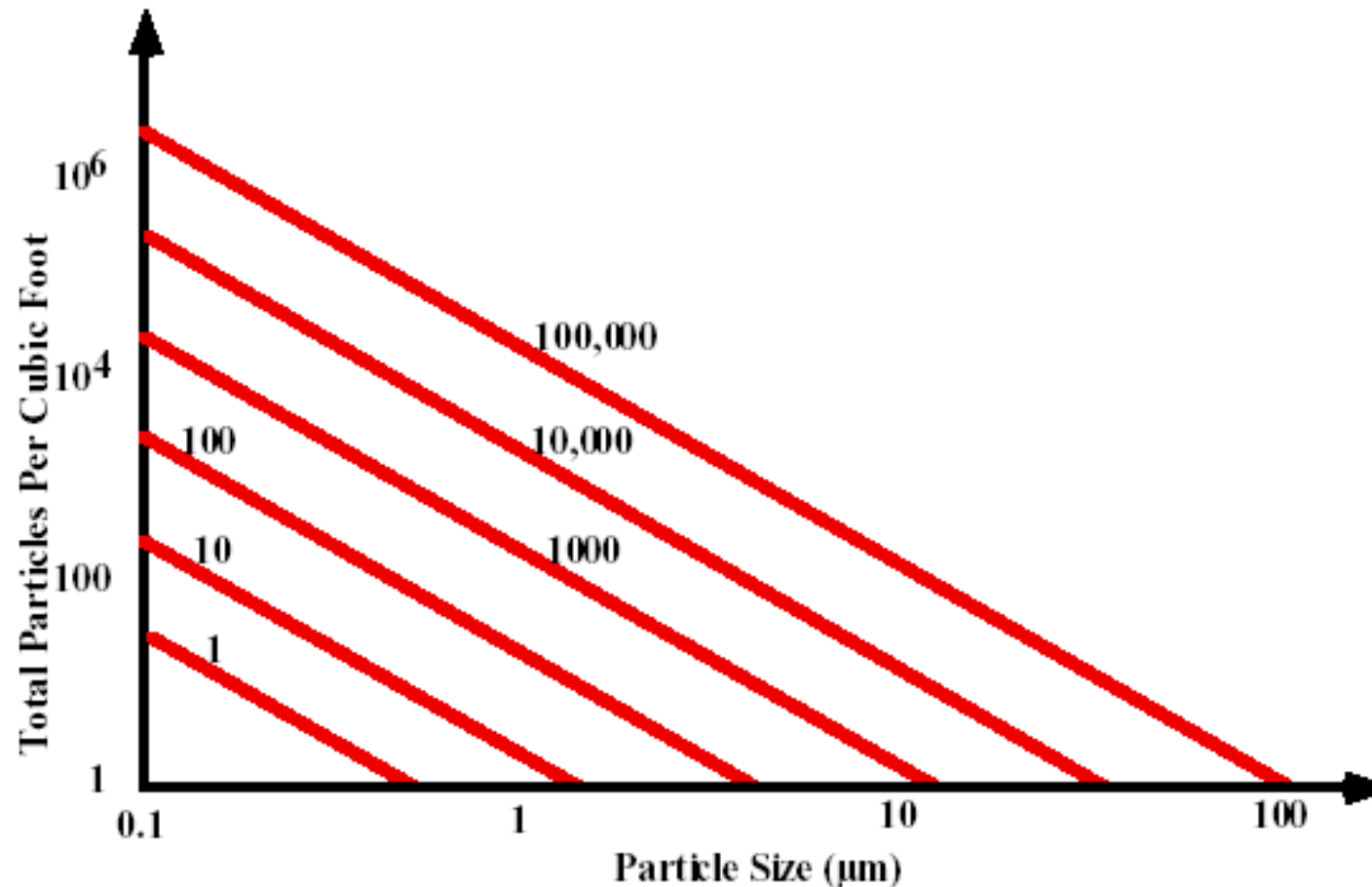
Cleanroom



class X:

less than X particles larger than $0.5\ \mu\text{m}$
per cubic feet

Cleanroom



class X:

less than **X** particles larger than $0.5 \mu\text{m}$
per cubic feet

Cleanroom

Particle Diameter (um)				
Class	0.1	0.3	0.5	5.0
1	35	3	1	
10	350	30	10	
100		300	100	
1,000			1,000	7
10,000			10,000	70
100,000			100,000	700

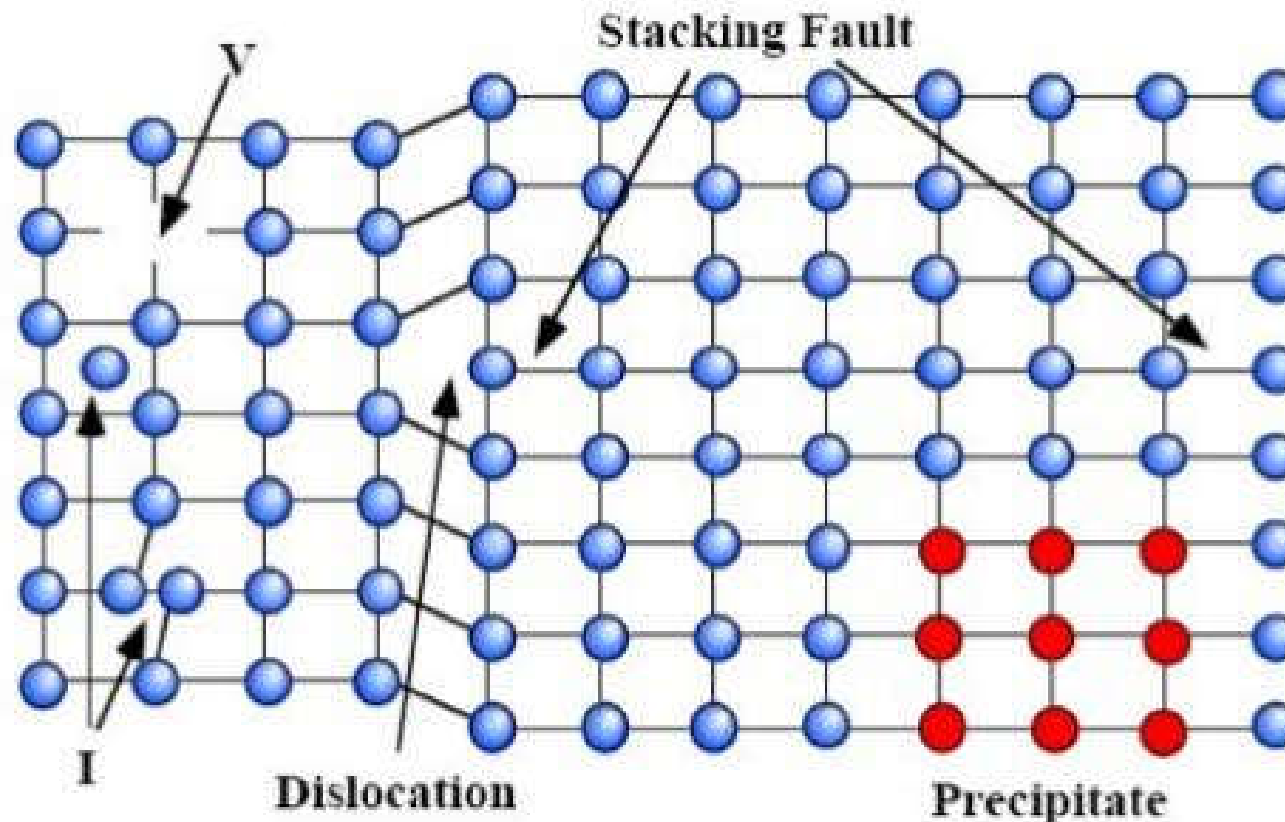
'PM2.5 index'
 $\ll 1 \mu\text{g}/\text{m}^3$

class X:

less than X particles larger than $0.5 \mu\text{m}$
 per cubic feet

Defects

- Point Defects e.g. Vacancies (V), Interstitials (I)
- Line Defects e.g. Dislocations
- Area Defects e.g. Stacking Faults (“extrinsic” or “intrinsic” form along {111} planes)
- Volume Defects e.g. Precipitates, Collection of Vacancies

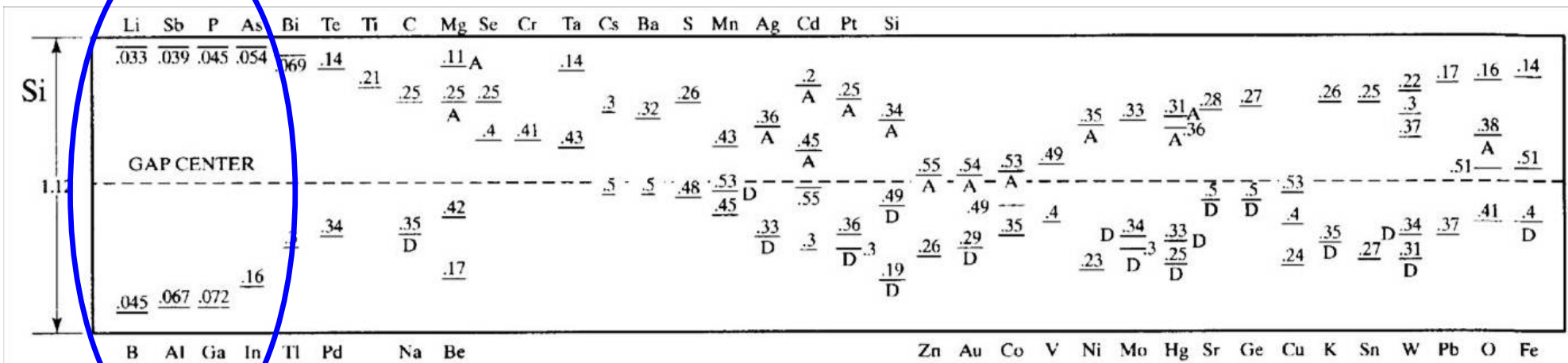


Defects

Q: why?

					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

dopants



deep level defects
Na, K, Au, Cu, Fe, O, ...

Defects

ions in gate oxide

dopants

deep level defects in Si

Periodic Table of the Elements

deep level defects in Si

Periodic Table of the Elements

1 1A 1A 1 H Hydrogen 1.008	2 2A 2A 4 Be Beryllium 9.012																	18 VIII 8A 2 He Helium 4.003																														
3 Li Lithium 6.941	10 Ne Neon 20.180																	10 Ne Neon 20.180																														
11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 B Boron 10.811	14 C Carbon 12.011	15 N Nitrogen 14.007	16 O Oxygen 15.999	17 F Fluorine 18.998	18 Ar Argon 39.948																																									
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.82																															
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29																															
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series		72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon 222.018																														
87 Fr Francium [223]	88 Ra Radium 226.025	89-103 Actinide Series		104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [277]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [272]	112 Cn Copernicium [285]	113 Uut Ununtrium [284]	114 Fl Flerovium [289]	115 Uup Ununpentium [288]	116 Lv Livermorium [293]	117 Uus Ununseptium [294]	118 Uuo Ununoctium [294]																														
<table><tr><td>57 La Lanthanum 138.905</td><td>58 Ce Cerium 140.115</td><td>59 Pr Praseodymium 140.908</td><td>60 Nd Neodymium 144.24</td><td>61 Pm Promethium 144.913</td><td>62 Sm Samarium 150.36</td><td>63 Eu Europium 151.966</td><td>64 Gd Gadolinium 157.25</td><td>65 Tb Terbium 158.925</td><td>66 Dy Dysprosium 162.50</td><td>67 Ho Holmium 164.930</td><td>68 Er Erbium 167.26</td><td>69 Tm Thulium 168.934</td><td>70 Yb Ytterbium 173.04</td><td>71 Lu Lutetium 174.967</td></tr><tr><td>89 Ac Actinium 227.038</td><td>90 Th Thorium 232.038</td><td>91 Pa Protactinium 231.036</td><td>92 U Uranium 238.029</td><td>93 Np Neptunium 237.048</td><td>94 Pu Plutonium 244.064</td><td>95 Am Americium 243.061</td><td>96 Cm Curium 247.070</td><td>97 Bk Berkelium 247.070</td><td>98 Cf Californium 251.080</td><td>99 Es Einsteinium [252]</td><td>100 Fm Fermium 257.095</td><td>101 Md Mendelevium 258.1</td><td>102 No Nobelium 259.101</td><td>103 Lr Lawrencium [262]</td></tr></table>																			57 La Lanthanum 138.905	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	89 Ac Actinium 227.038	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [252]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]
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Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide																																							

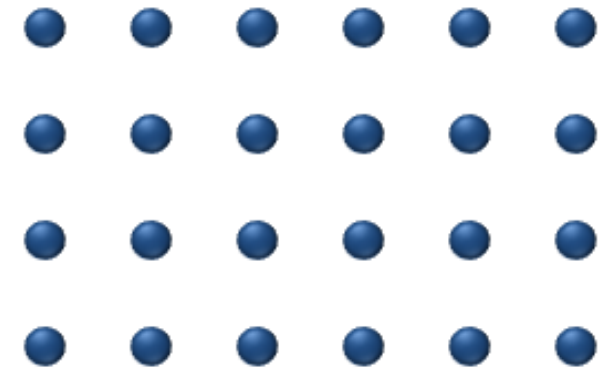
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Diffusion of Defects

Liquid



Solid



C concentration (mol/m^3)

J diffusion flux ($\text{mol/m}^2/\text{s}$)

D diffusivity (m^2/s)

Diffusion of Defects

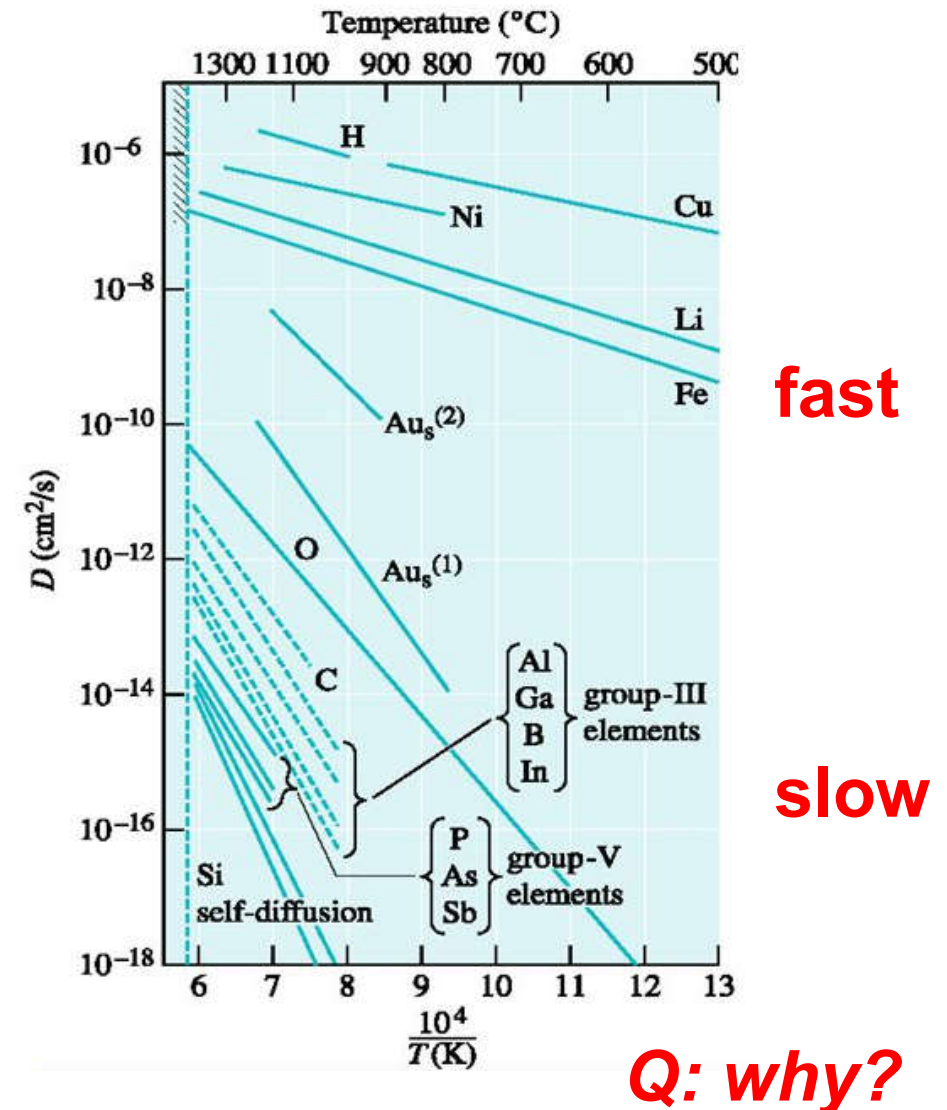
■ Diffusivity (扩散系数) D

- rate of spread
- unit: cm^2/s

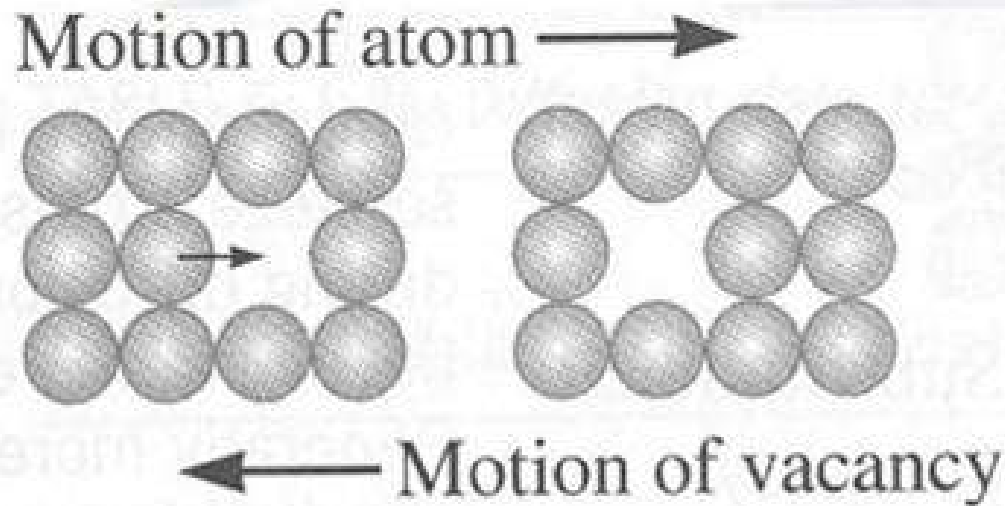
$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

■ Diffusion length L

$$L = \sqrt{Dt}$$

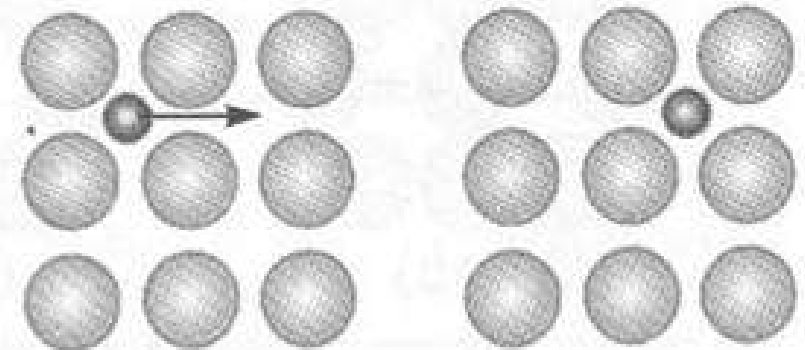


Defect Diffusivity in Silicon



(a) Vacancy mechanism

B, P, As, Sb, Si, ...



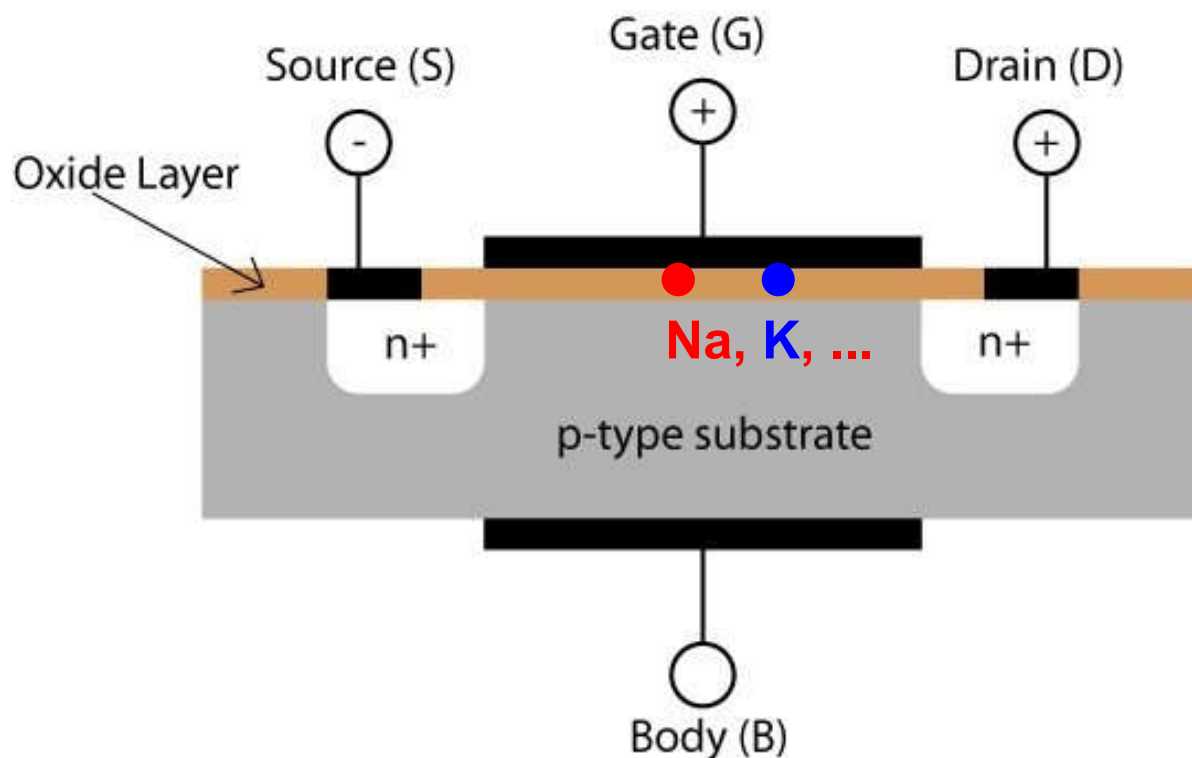
(b) Interstitial mechanism

Cu, Fe, Li, H, Au, ...

Defects

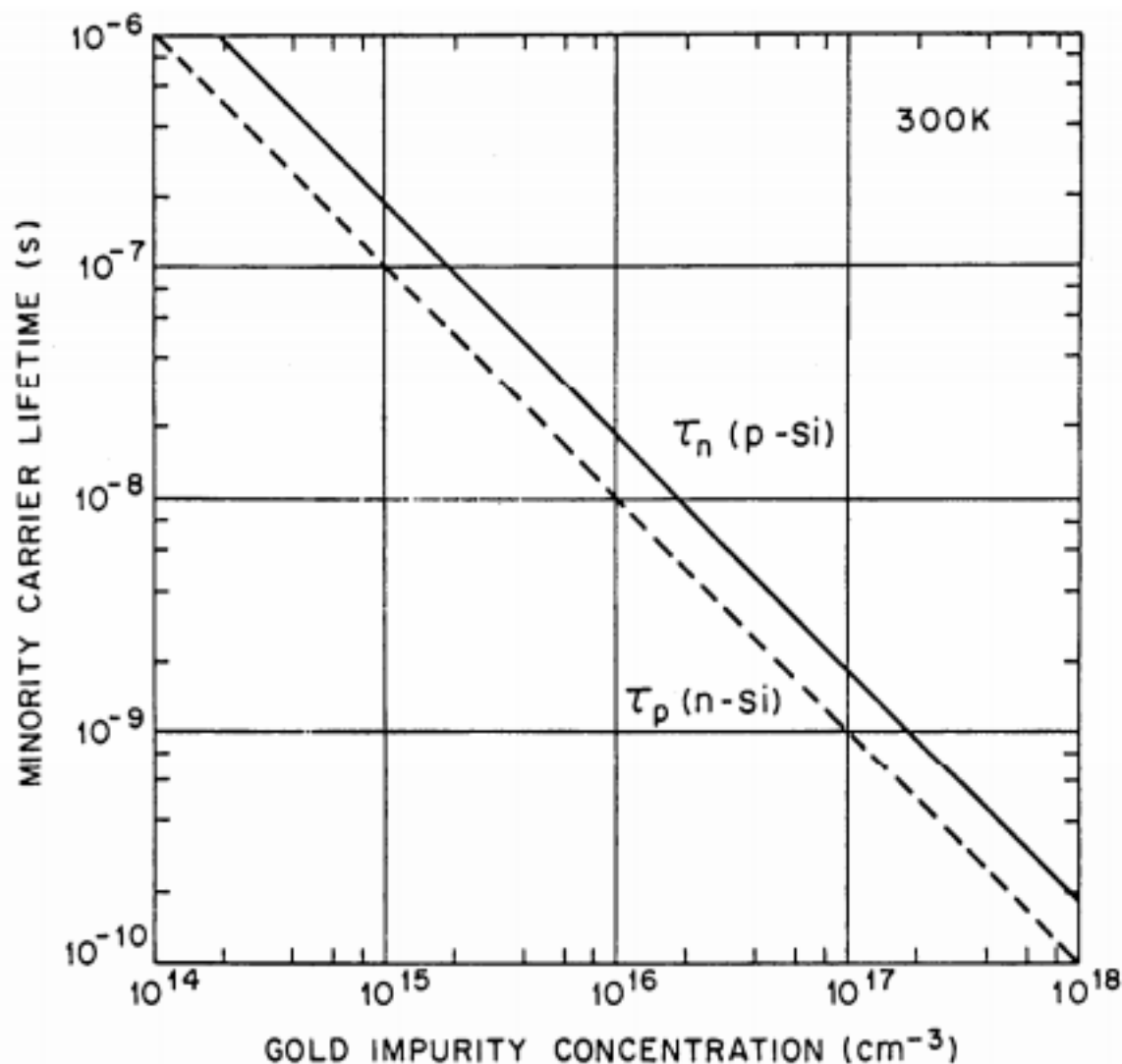
$$V_{th} = V_{FB} + 2\Phi_f + \frac{\sqrt{2\varepsilon_s q N_A (2\Phi_f)}}{C_{ox}} - \frac{qQ_M}{C_{ox}}$$

defect density



alkali ions (Na, K, ...)
in gate oxide

Defects



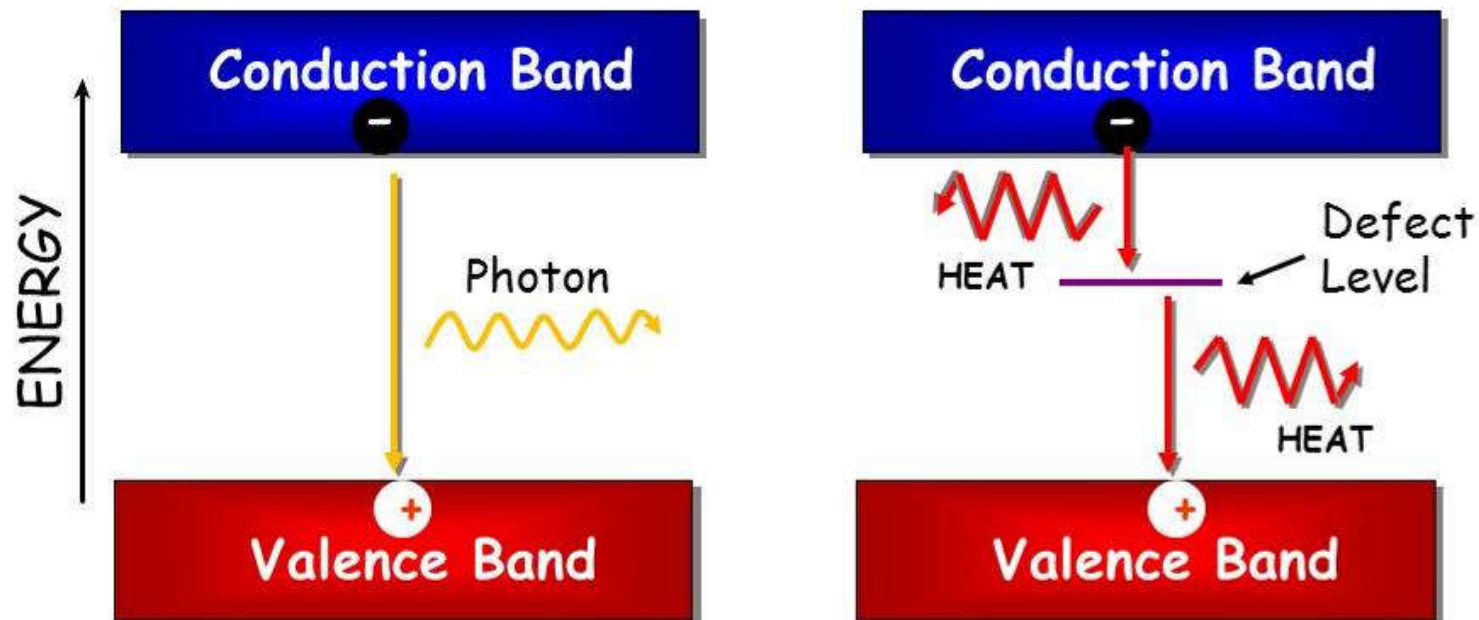
**Deep level defects
(e.g. Au) reduce
minority carrier
lifetime**

bad for solar cells

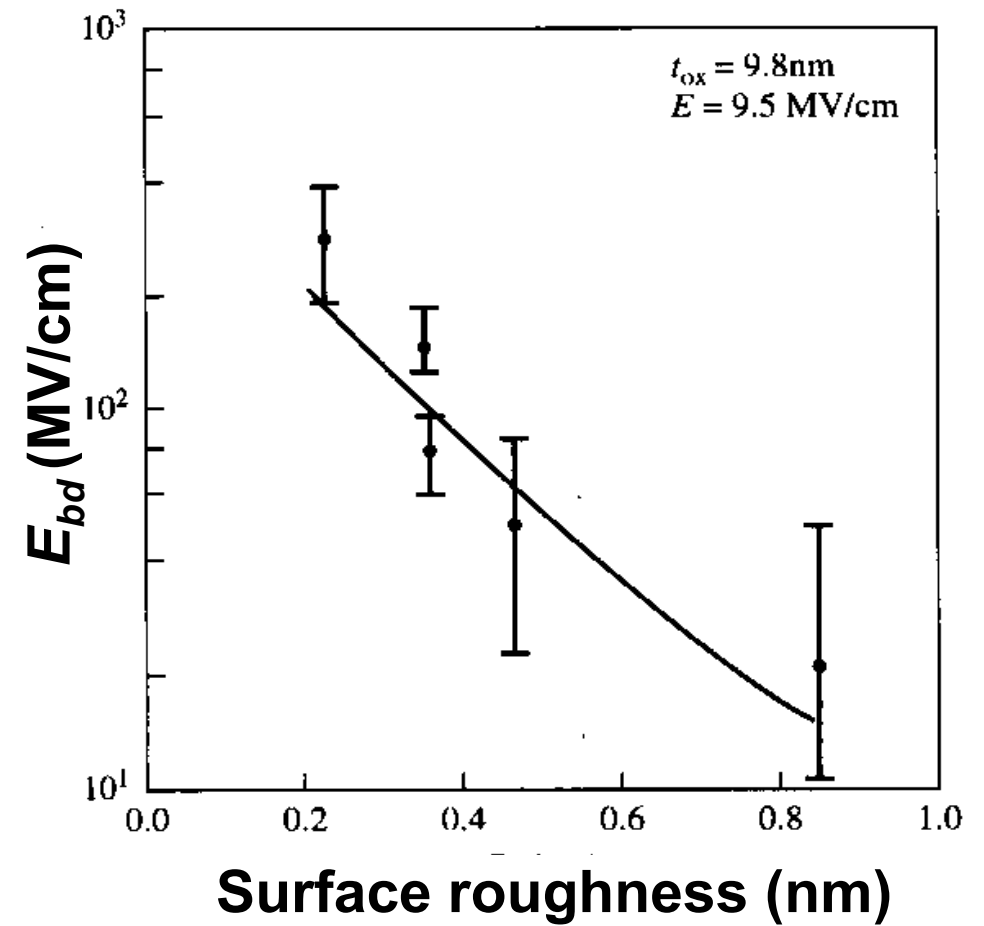
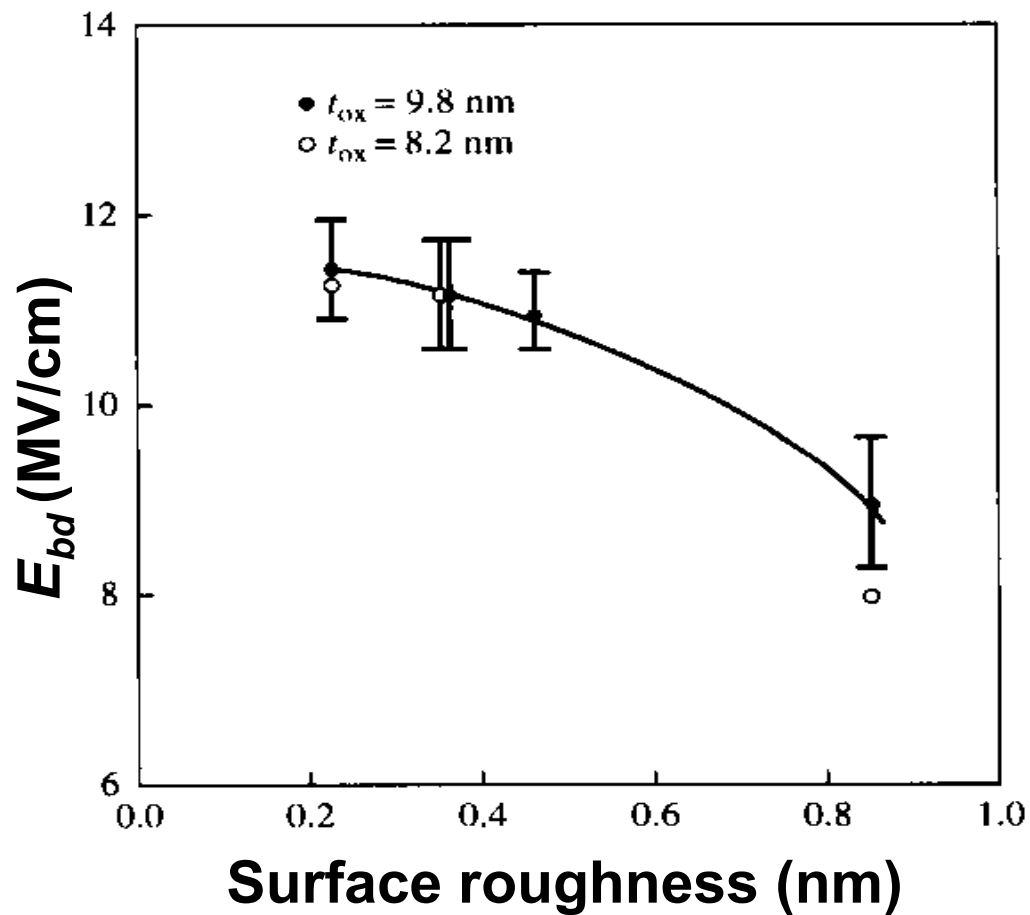
Fig. 16 Recombination lifetime versus gold impurity concentration in silicon.⁸

Defects

recombination at defect sites
reduce efficiencies of LEDs / solar cells



Defects



Surface roughness reduces breakdown voltages (E_{bd})

Defects

defects in water



effects of water cleaning on transistor performance

water resistivity ($M\Omega \cdot \text{cm}$, at 25 °C)	leakage current ($\text{A}/\mu\text{m}^2$)
5	$12 \cdot 10^{-9}$
10	$10 \cdot 10^{-9}$
13	$5 \cdot 10^{-9}$
15	$1 \cdot 10^{-9}$

Water

■ Types

- purified water, distilled water, tapping water, ...
- 自来水, 矿泉水, 纯净水, 超纯水, 蒸馏水, ...

■ In cleanroom, **deionized (DI) water (去离子水)** is used

- free of any mineral ions
- only H^+ , OH^-



■ In water, at 25 °C

- $[H^+][OH^-] = K_w = 10^{-14} \text{ (mol/L)}^2$
- in DI water, $[H^+] = [OH^-] = 10^{-7}$, **pH = 7.0**
- resistivity = **18.5 MΩ*cm**

Defects Control

environment ← **cleanroom control**

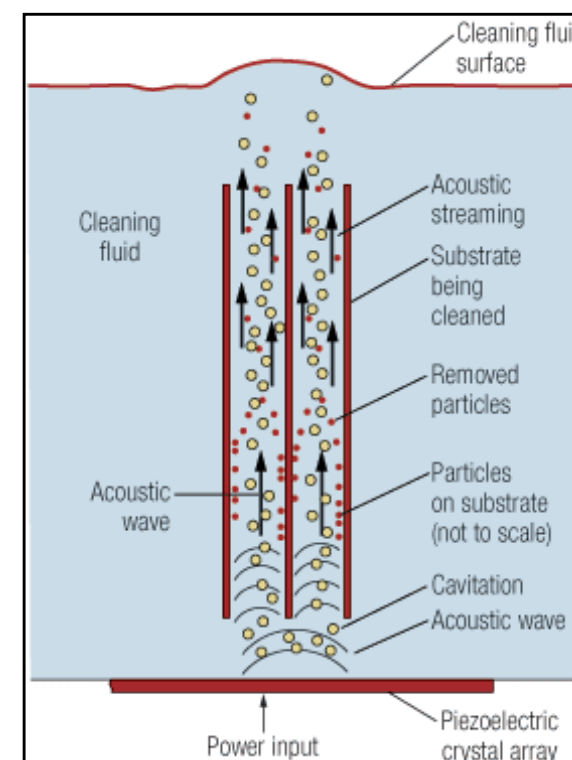
← **surface clean**

← **gettering**

Si wafer

Si Wafer Clean

- Ultrasonic / megasonic clean in DI water



**remove: large particles,
water soluble ions (Na, K, Cl, ...)**

Standard Si Wafer Clean (RCA)

■ Step 1 (SC-1)

- $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1:1:5$, at 80 °C, 10 mins
- remove organic residues

■ Step 2

- $\text{HF} : \text{H}_2\text{O} = 1:50$, at 25 °C, 20 secs
- remove native SiO_2

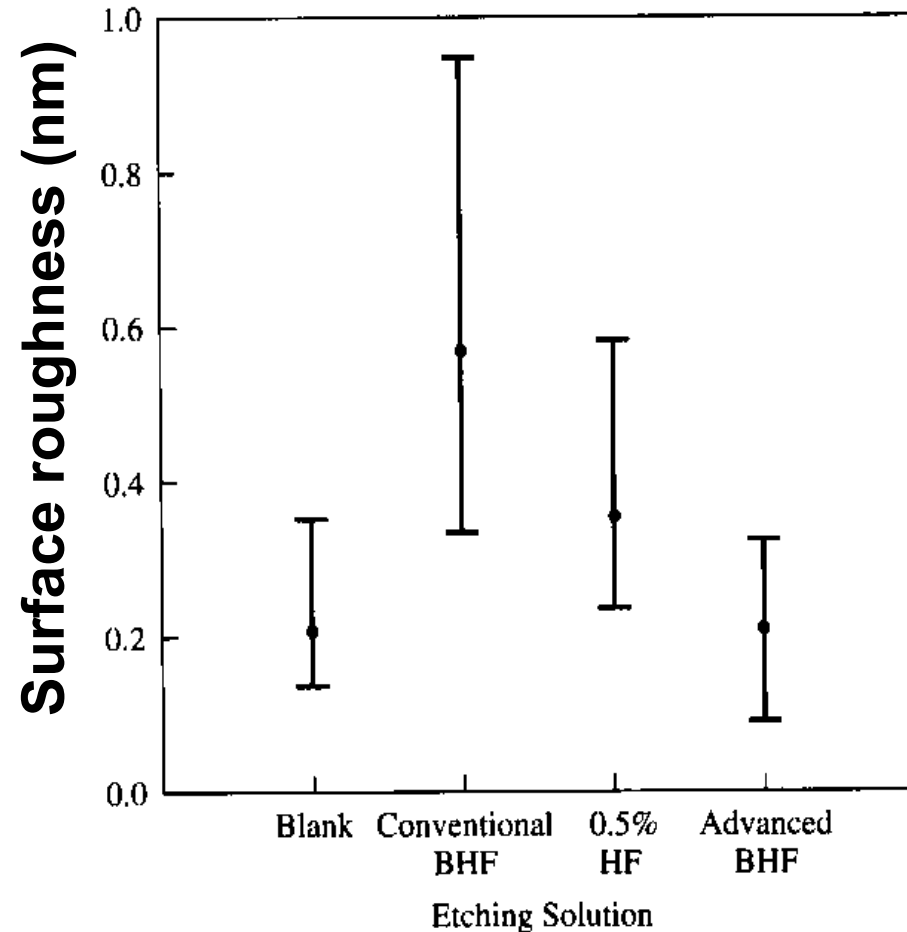
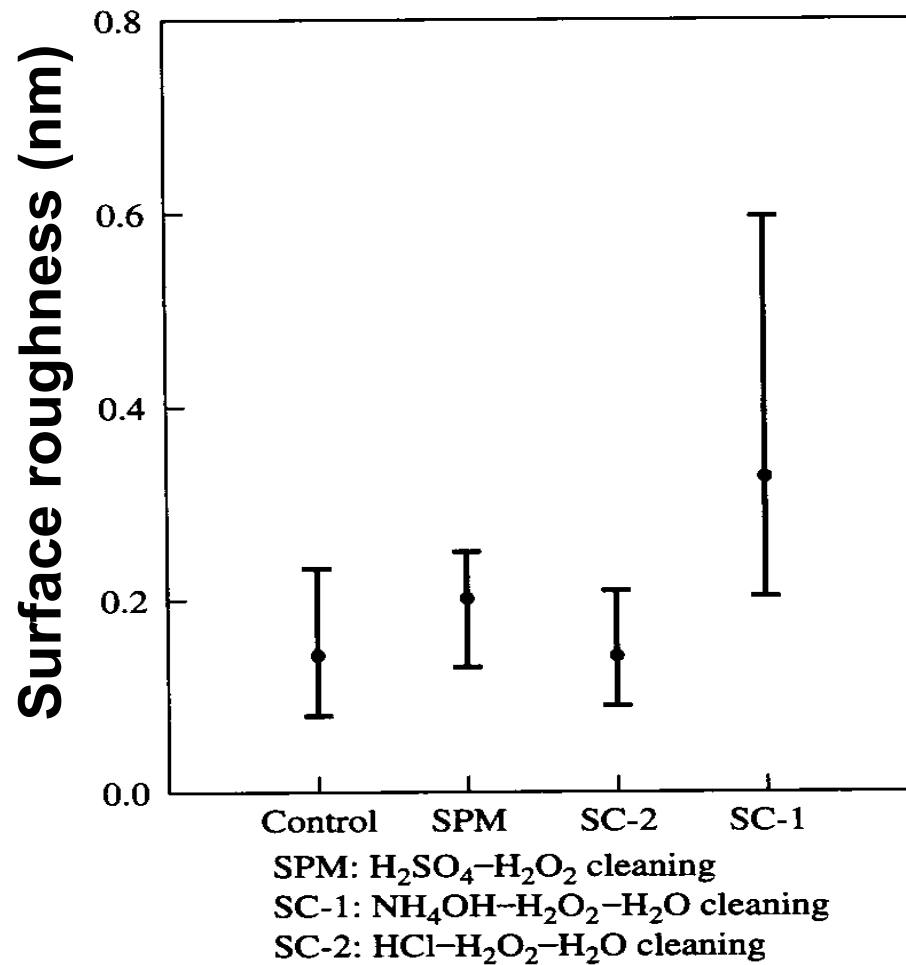
■ Step 3 (SC-2)

- $\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1:1:6$, at 80 °C, 10 mins
- remove metals

■ Step 4

- clean in DI water

Surface Roughness



Surface Roughness of Si after cleaning ammonia (NH_4OH) and HF slightly etches Si

Metal Removal

Table 4-3 Oxidation-reduction reactions for a number of species of interest in silicon wafer cleaning

Oxidant/ Reductant	Standard Oxidation Potential (volts)	Oxidation-Reduction Reaction
Mn ²⁺ /Mn	1.05	$\text{Mn} \leftrightarrow \text{Mn}^{2+} + 2\text{e}^-$
SiO ₂ /Si	0.84	$\text{Si} + 2\text{H}_2\text{O} \leftrightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e}^-$
Cr ³⁺ /Cr	0.71	$\text{Cr} \leftrightarrow \text{Cr}^{3+} + 3\text{e}^-$
Ni ²⁺ /Ni	0.25	$\text{Ni} \leftrightarrow \text{Ni}^{2+} + 2\text{e}^-$
Fe ³⁺ /Fe	0.17	$\text{Fe} \leftrightarrow \text{Fe}^{3+} + 3\text{e}^-$
H ₂ SO ₄ /H ₂ SO ₃	-0.20	$\text{H}_2\text{O} + \text{H}_2\text{SO}_3 \leftrightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 4\text{e}^-$
Cu ²⁺ /Cu	-0.34	$\text{Cu} \leftrightarrow \text{Cu}^{2+} + 2\text{e}^-$
O ₂ /H ₂ O	-1.23	$2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
Au ³⁺ /Au	-1.42	$\text{Au} \leftrightarrow \text{Au}^{3+} + 3\text{e}^-$
H ₂ O ₂ /H ₂ O	-1.77	$2\text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
O ₃ /O ₂	-2.07	$\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{O}_3 + 2\text{H}^+ + 2\text{e}^-$



Other Si Clean Recipes

■ Piranha clean

- ❑ SPM: Sulfuric-Peroxide Mixture
- ❑ $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 3:1$, 10–30 mins
- ❑ extremely exothermic, self heating up to 80 °C
- ❑ remove organic residues and some metals



DANGER

■ Ozone (O_3) clean

- ❑ $\text{H}_2\text{O} + \text{O}_3$
- ❑ remove organic residues

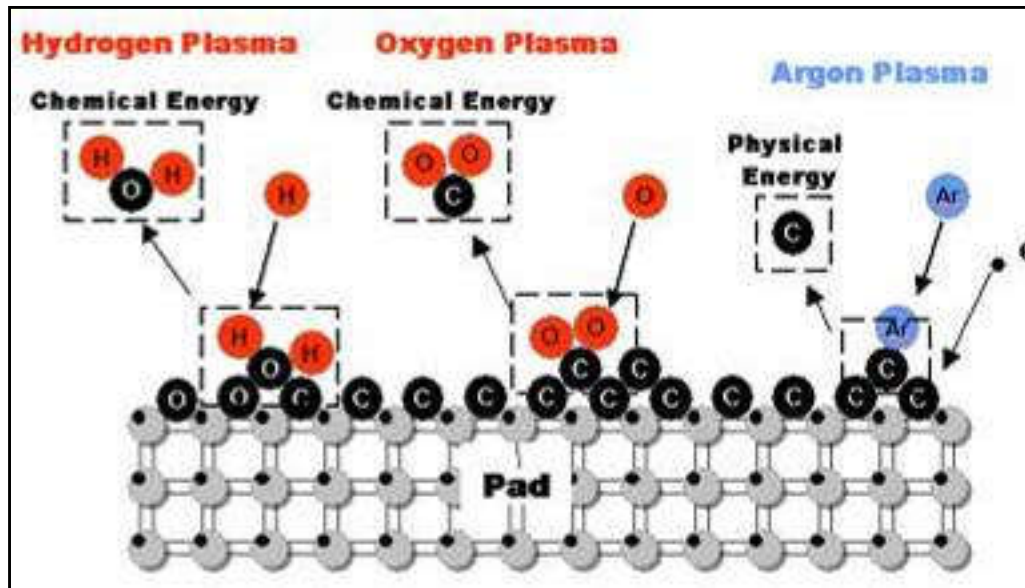
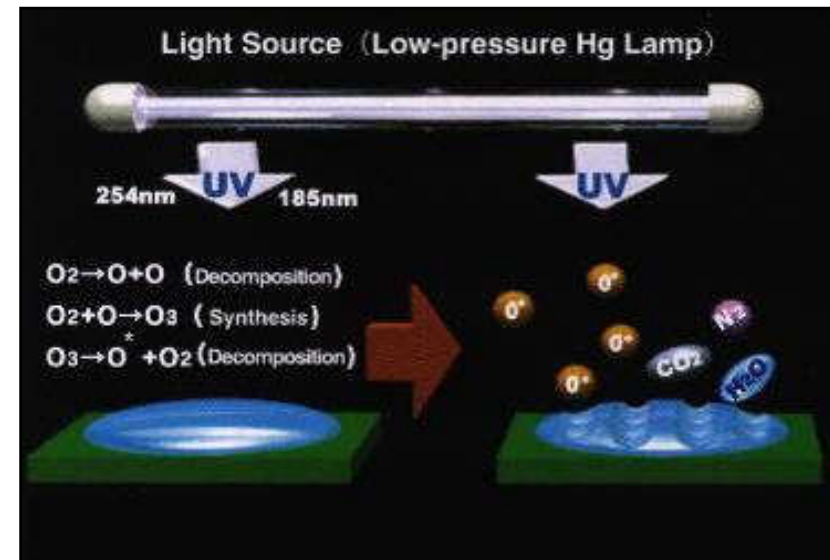
■ Organic solvent

- ❑ Acetone / Isopropanol / DI water
- ❑ remove organic residues
- ❑ not used for standard CMOS process!

'wet' method

Other Si Clean Recipes

- UV Ozone clean
 - clean organic residues
- Plasma clean
 - clean organic residues



'dry' method

Clean other Materials

- **SiO₂ (glass, quartz, ...)**
 - piranha clean, $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 3:1$, 10–30 mins

- **GaAs**
 - $\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1:10$, for stoichiometric surface (Ga/As 1:1)
 - H_3PO_4 or HCl , for As rich surface

- **Acetone / Isopropanol / DI water**
 - generally works well for most non-CMOS process

Defects Control

environment ← **cleanroom control**

← **surface clean**

← **gettering**

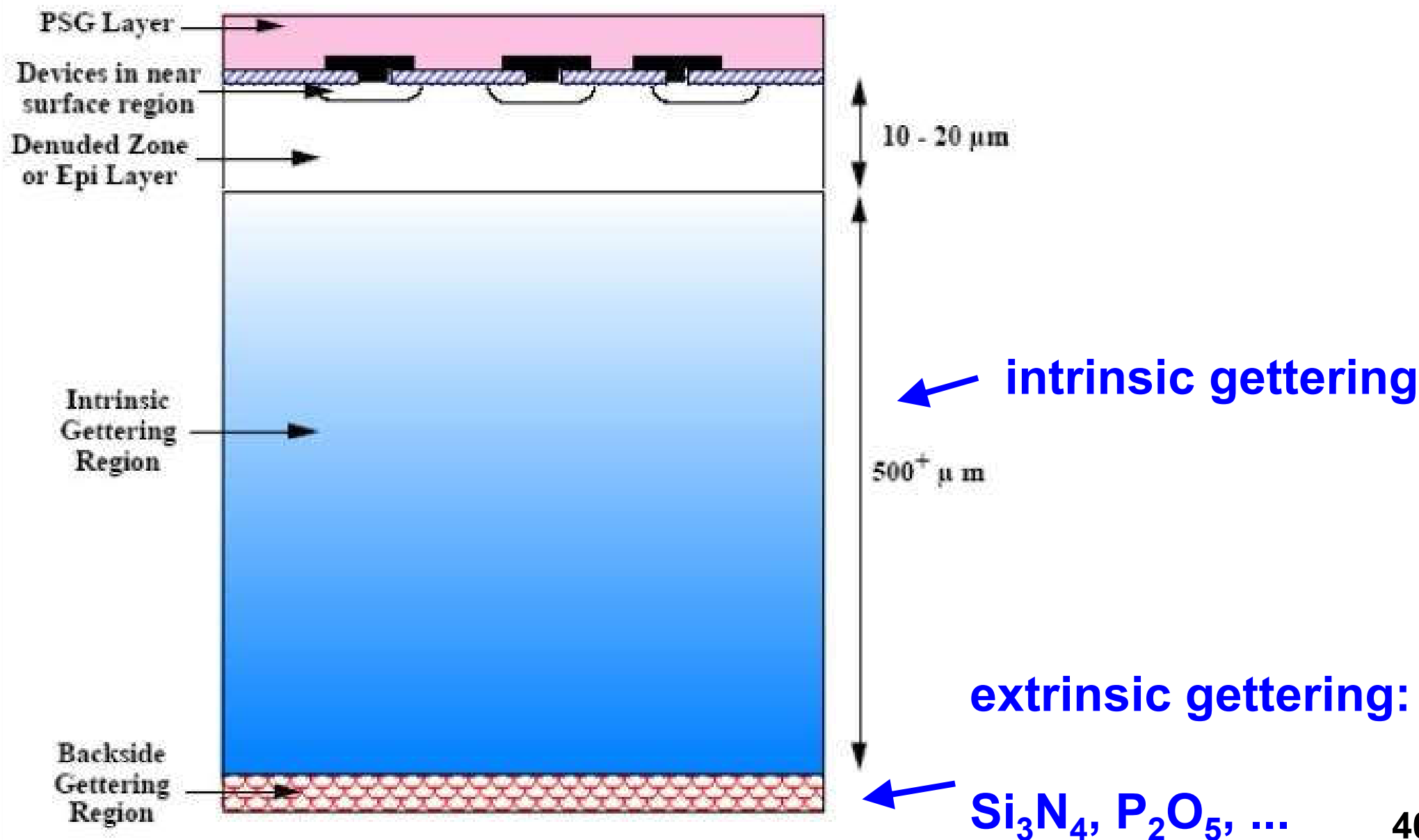
Si wafer

Si Wafer Gettering (吸杂)

- 'gettering' in vacuum
 - use titanium to absorb gases in vacuum tubes

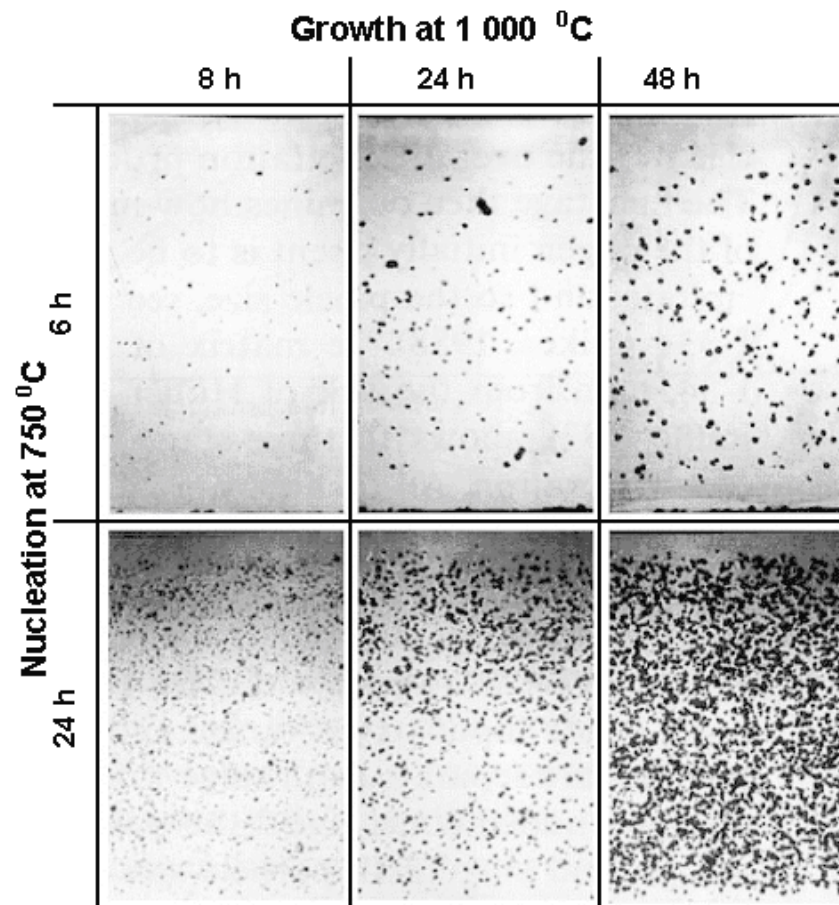


Si Wafer Gettering (吸杂)

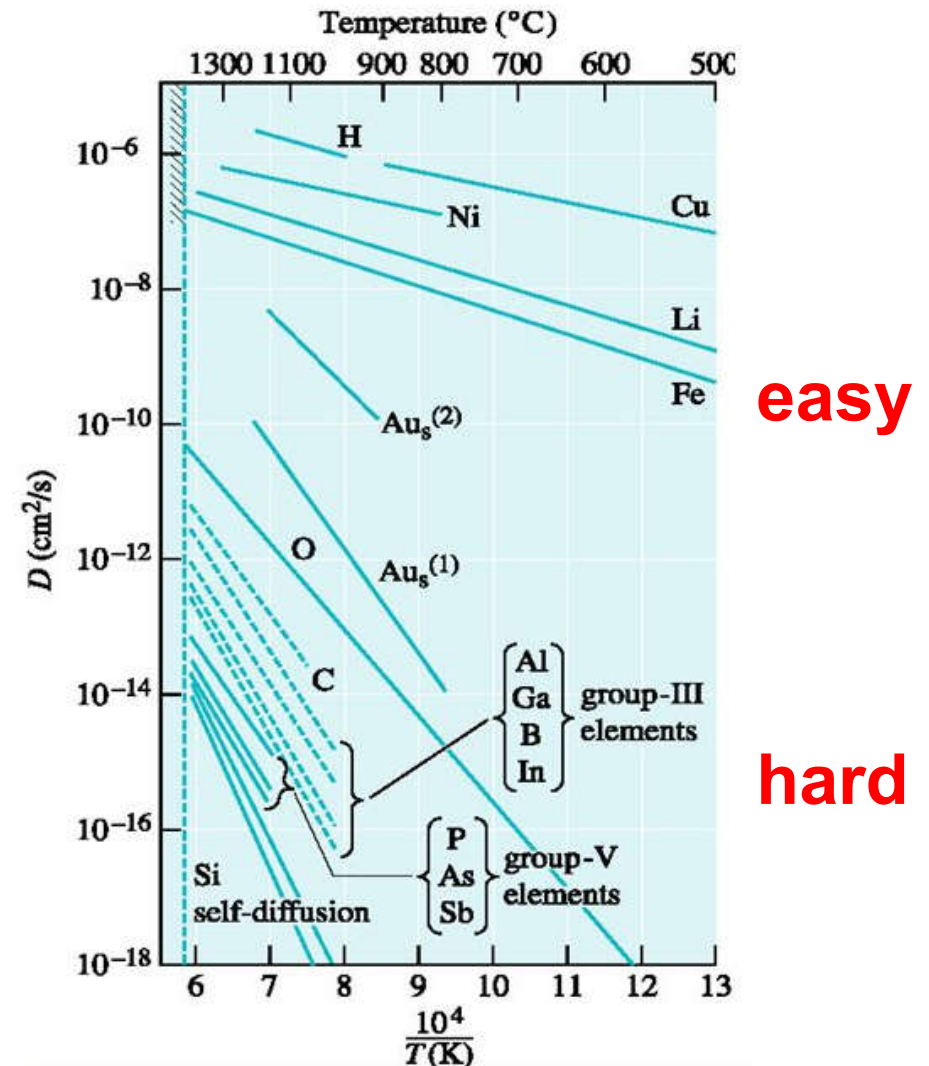


Si Wafer Gettering (吸杂)

■ intrinsic gettering



O defects in Si



diffusivity of defects

Si Wafer Gettering (吸杂)

- Minority carrier lifetime

Au doped Si: 10^{-9} s

Typical Si: 10^{-6} s

Gettered Si: 10^{-3} s

Lab Safety

- **Chemicals**

- HF , H_2SO_4 , ...
- KOH , NH_4OH , ...
- Acetone, ...



- **Electricity**

- instruments, ...



- **Fires**

- Acetone, Alcohol, ...

- **Sharps**

- silicon, glass, ...

- ...



Lab Safety

- Lab orientation

- exits, showers, ...

- Proper protection

- gloves, goggles, aprons, ...



- Materials Data Safety Sheets (MSDS)

- ...



Lab Safety

■ Materials Data Safety Sheets (MSDS)

Material Safety Data Sheet Hydrofluoric Acid, 48% MSDS

Section 1: Chemical Product and Company Identification

Product Name: Hydrofluoric Acid, 48%

Catalog Codes: SLH2227

CAS#: 7664-39-3

RTECS: Not applicable.

Contact Information:

Sciencelab.com, Inc.

14025 Smith Rd.


Houston, Texas 77396

US Sales: 1-800-901-7247

International Sales: 1-281-444-4400

Section 3: Hazards Identification

Potential Acute Health Effects:



Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Chemical Safety

■ NFPA diamond

- 0: no hazard
- 4: highest risk



HF



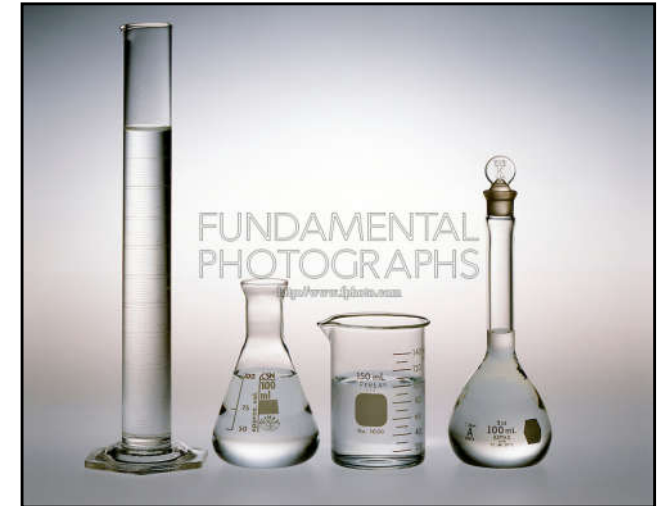
acetone



H₂O₂

Chemical Safety

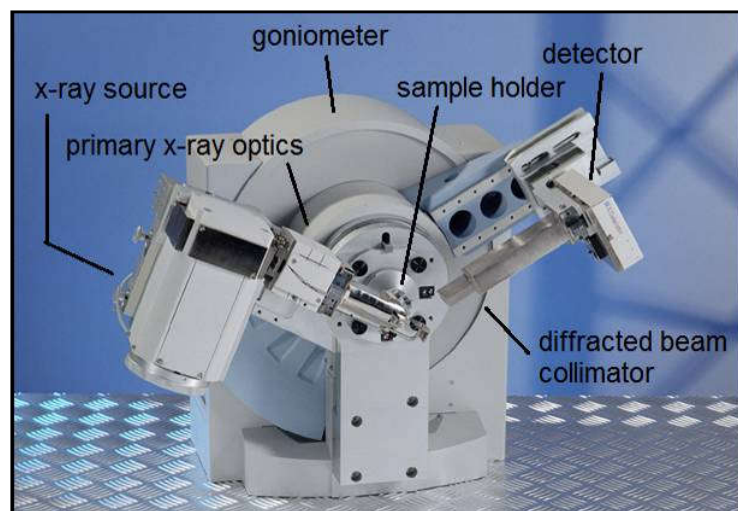
- Choose proper containers
- Most solvents
 - glass, Teflon, ...
- Be careful
 - alkali (NaOH, etc) slowly etches glass
 - HF strongly etches glass!



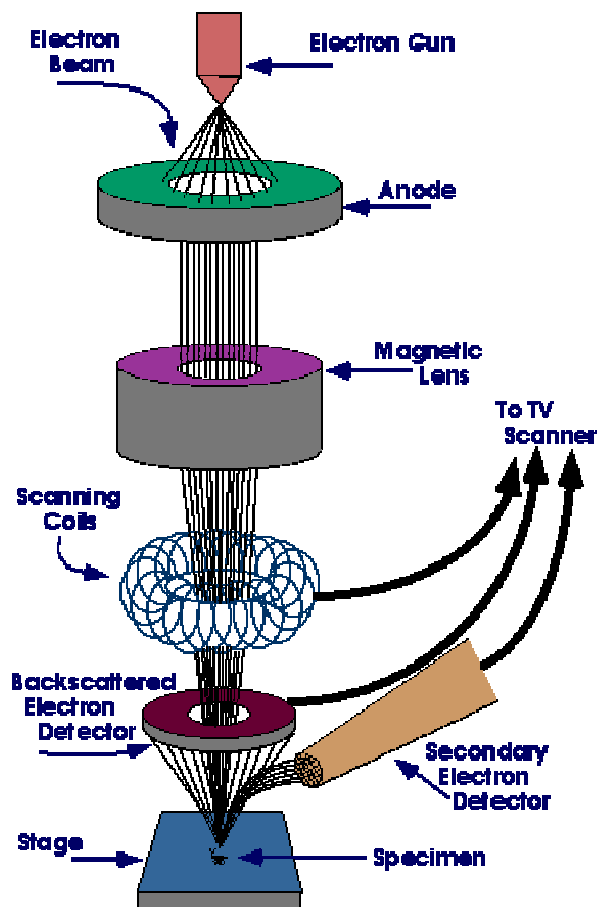
glass art by HF etch



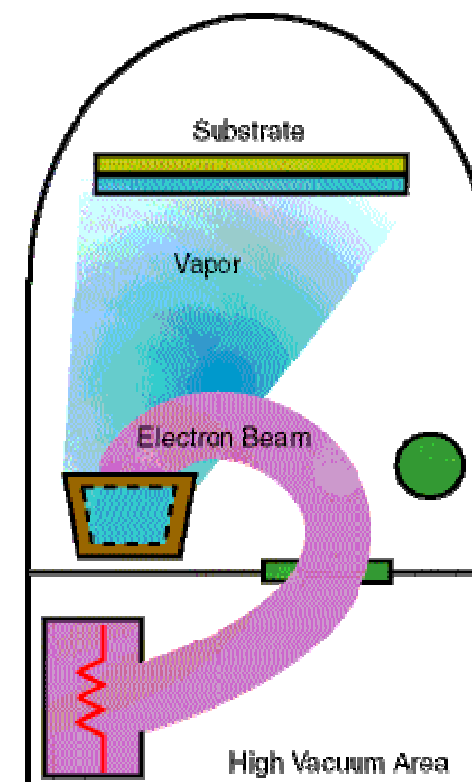
Radiation Safety



XRD



SEM & TEM



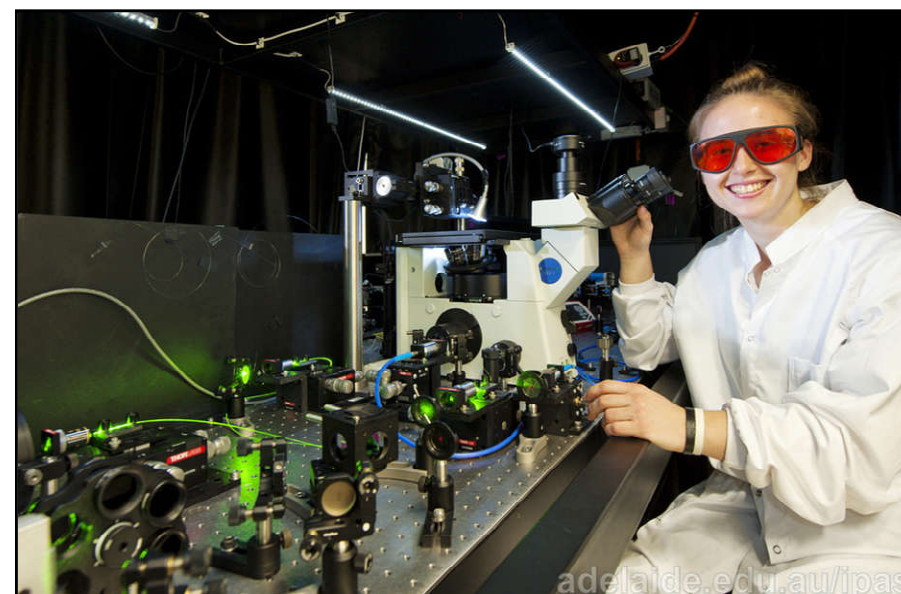
Ebeam Evaporator

Laser Safety

Class 1	CD/DVD Player/Recorder, Laptop or Personal Computer
Class 2	Presentation Laser Pointer, Barcode Reader
Class 3R	Some Measuring & Targeting Devices, Higer Power Pointers
Class 3B	Higher power laser products intened for professional applications
Class 4	Medical Lasers, Industrial Cutting/Welding, Scientific Applications and most <i>Laser Light Show</i> Equipment



wear goggles



Biological Safety



↑
**Basic
Facility**
↓

- BSL-1
 - Safe microorganisms
 - Not known to cause disease in healthy adult humans
- BSL-2
 - Moderate-risk microorganisms
 - Potentially hazard to humans and the environment
 - e.g. inactivated virus that Causes Foot and Mouth Disease

↑
**Containment
Facility**
↓

- BSL-3, BSL-3 Enhanced & BSL-3 Ag
 - High-risk microorganisms, foreign and emerging agents
 - Serious and potential lethal consequences for livestock
 - Not harmful to humans because of protective measures
 - e.g. live virus that Causes Foot and Mouth Disease
- BSL-4
 - High-risk agents microorganisms
 - No known vaccine or therapy
 - e.g. Nipah and Hendra viruses

Thank you for your attention