Semiconductor Manufacturing Technology

Michael Quirk & Julian Serda

Chapter 5

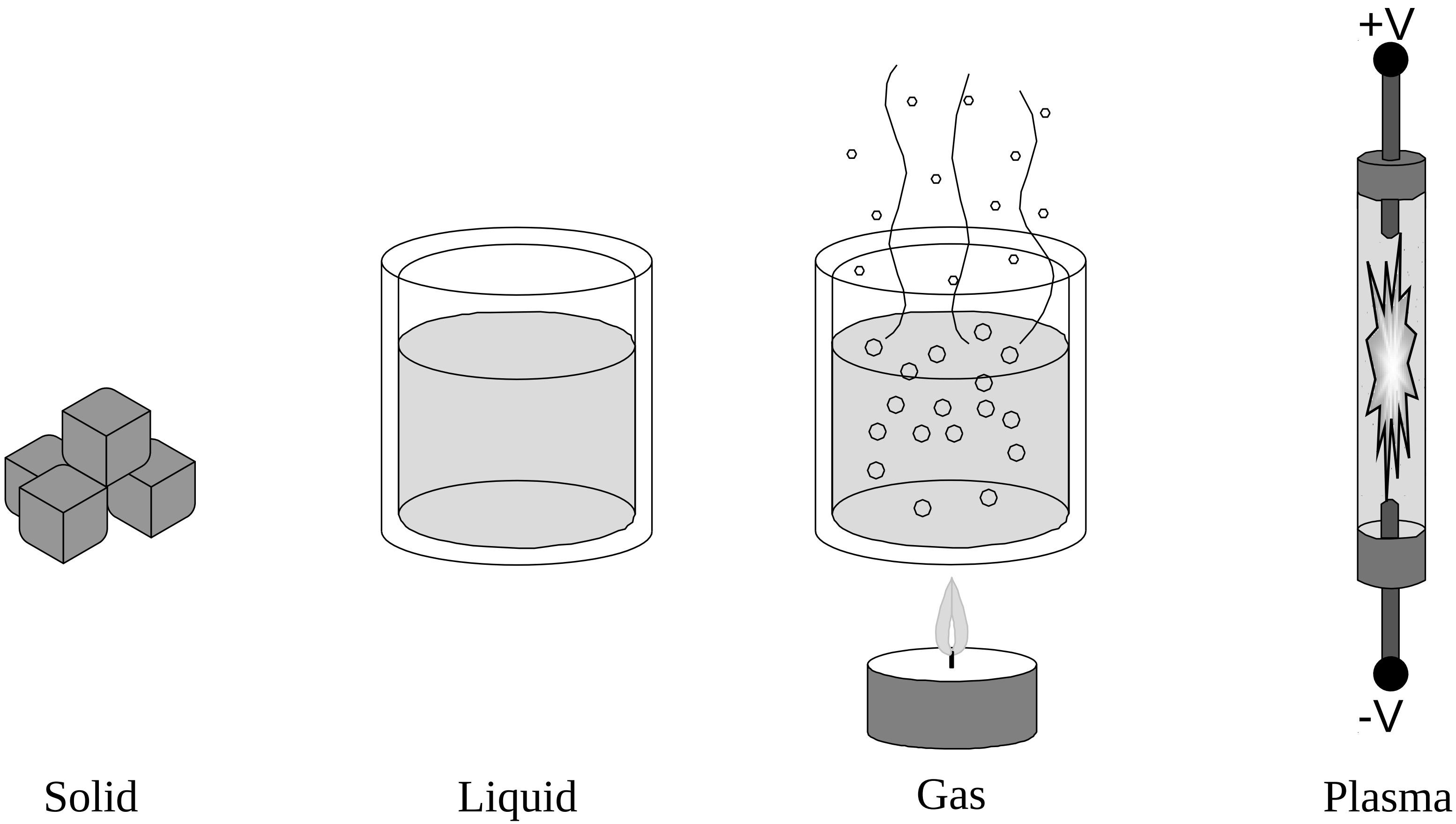
Chemicals in Semiconductor Fabrication

Objectives

After studying the material in this chapter, you will be able to:

1. Identify and discuss the four states of matter.
2. Describe the important chemical properties relevant to semiconductor manufacturing.
3. State how the different process chemicals are categorized and used in a wafer fab.
4. Explain how an acid, base and solvent are used in chip manufacturing.
5. State whether a gas is a bulk or specialty gas and how each type of gas is delivered and used in wafer fabrication.

Physical States of Matter



- Inert gases (He, Ar, or N_2) are widely used in semiconductor manufacturing because they do not react with other chemical
- Plasma: high energy collection of ionized molecules or atom, e.g., star, fluorescent light, and neon signs

Figure 5.1

Properties of Materials

- Identifying properties for materials used in semiconductor manufacturing is important for understanding how to properly fabricate the silicon wafer to build chips.
- Physical properties: reflect a material by itself without its interacting with another substance: melting point, boiling point, resistance…
- Chemical properties: flammability, reactivity, and corrosiveness (from reactance to product)

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Temperature Scales

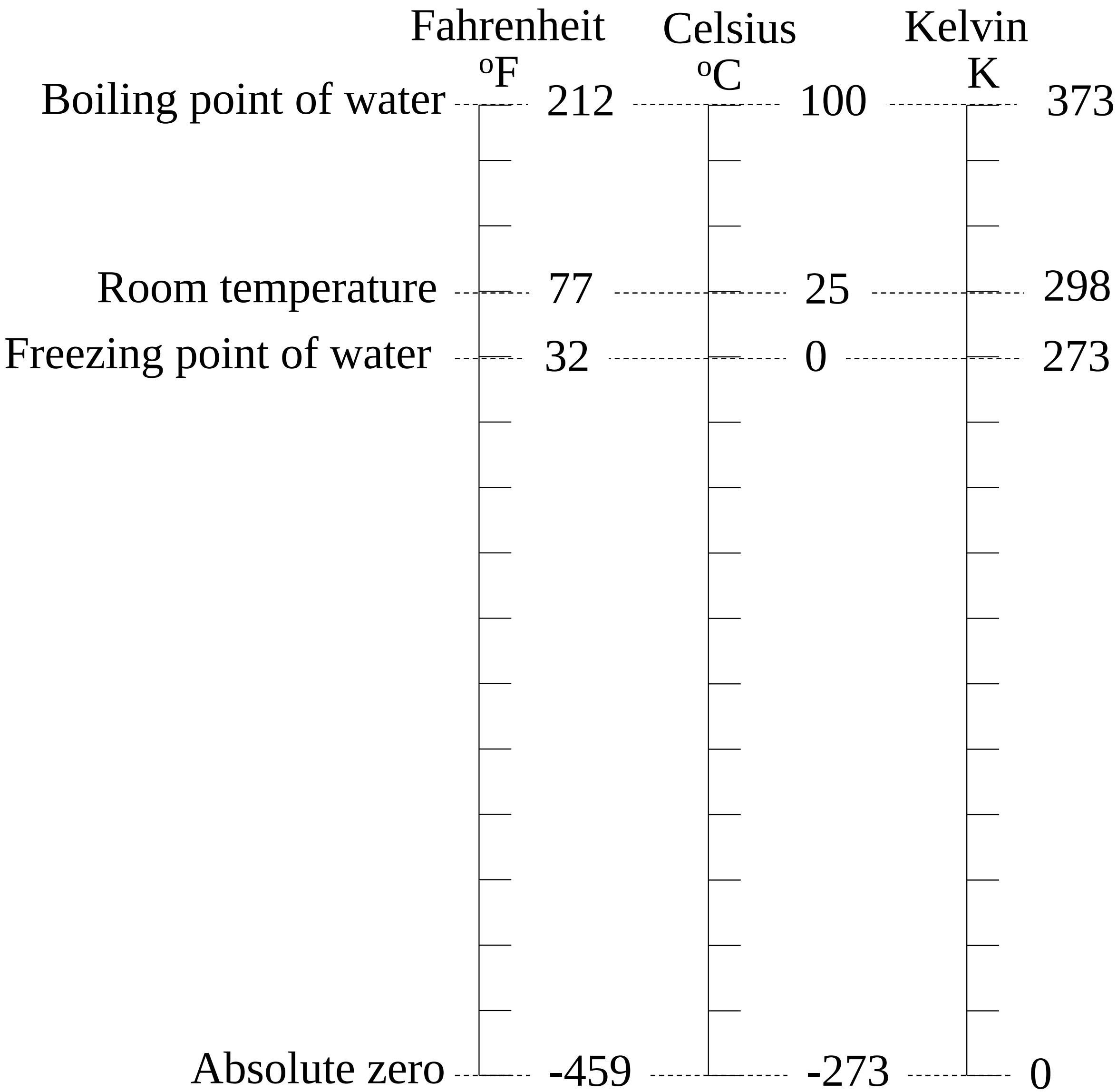


Figure 5.2

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Pressure Against a Container Wall

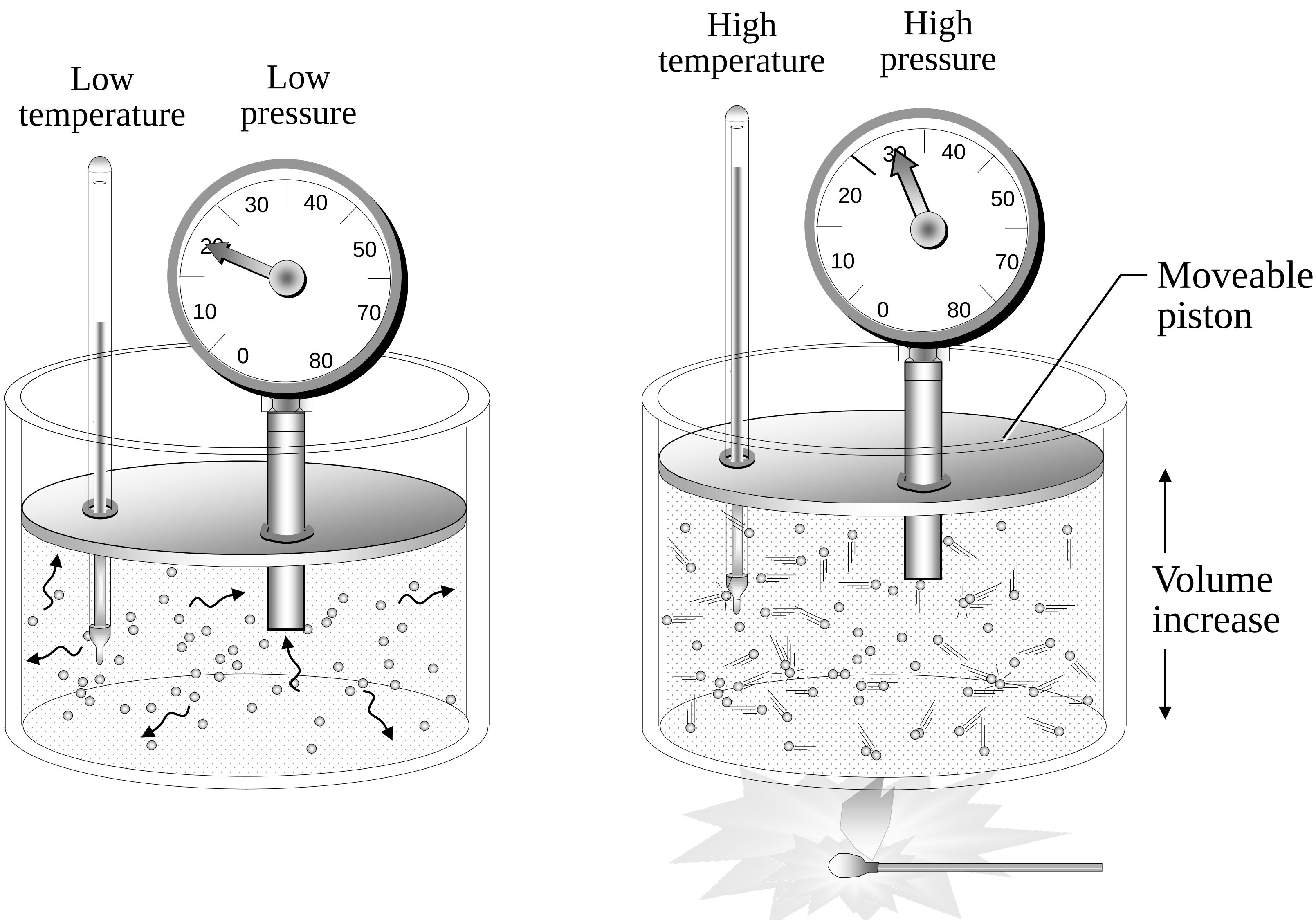


Figure 5.3

Gauge Pressure (psig) Versus Absolute Pressure (psia)

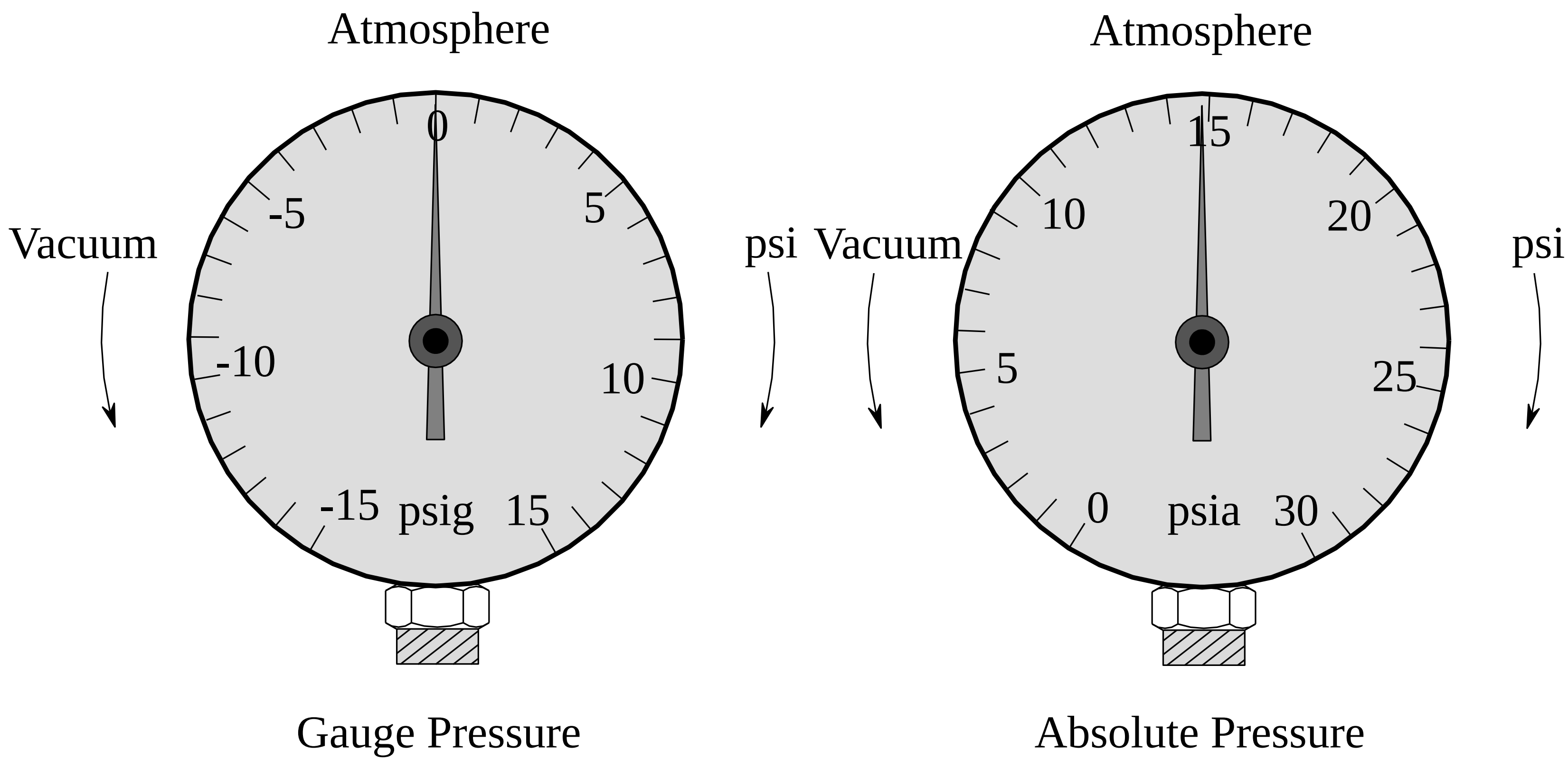


Figure 5.4

Units of Pressure at Sea Level and 23°C

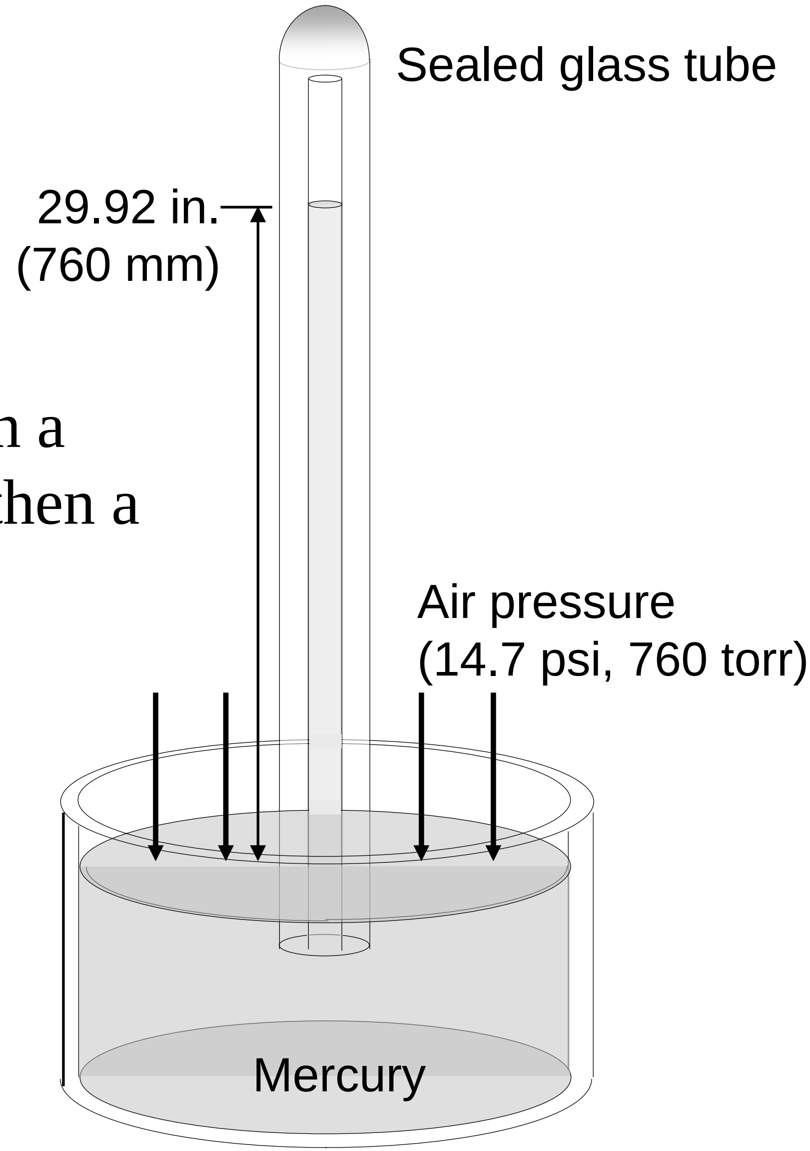
Standard Atmospheric Pressure at Sea Level and 23°C	
Psig (gauge)	0 psi
Psia (absolute)	14.7 psi
Atmosphere	14.7 psi
Inches of mercury	29.92 inches
Millimeters of mercury	760 mm
Torr	760 torr
Mtorr	760,000 mtorr
Bar	1.013 bar
Millibar	1013 mbar
Pascal	101,325 pascal

Table 5.1

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Barometer at Atmospheric Pressure



- If the gas pressure in a container < 1 atm., then a vacuum exists.

Figure 5.5

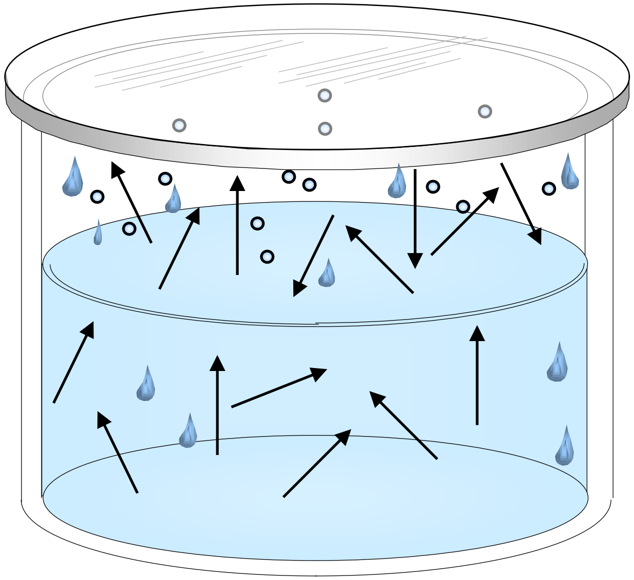
Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation (gas → liquid)
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure (vaporization vs. condensation)
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Vapor Pressure



High vapor pressure materials are *volatile*, e.g., solvents, perfumes, and lotions

Figure 5.6

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Sublimation

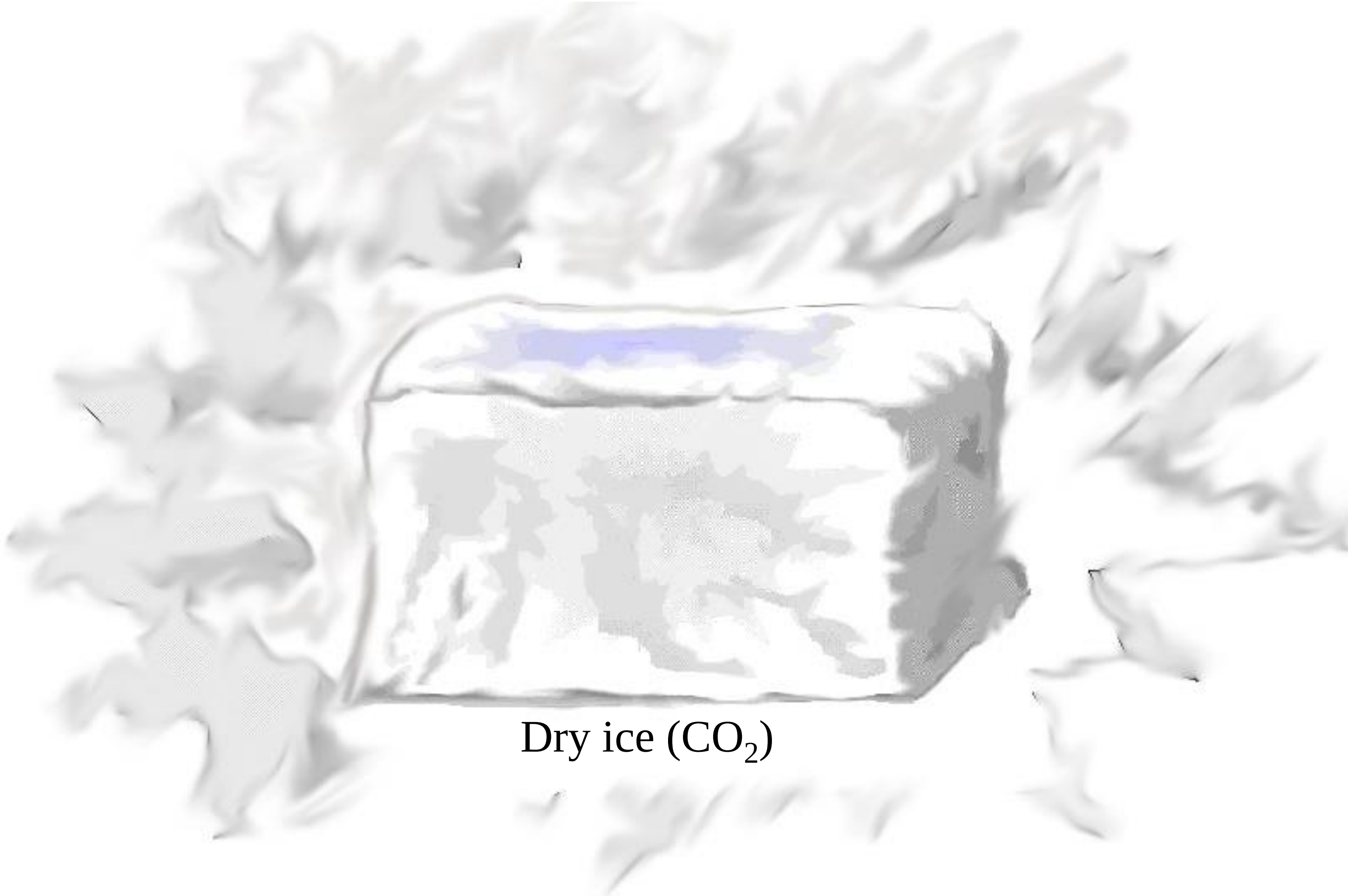


Figure 5.7

Deposition
v.s. sublimation (gas to solid)

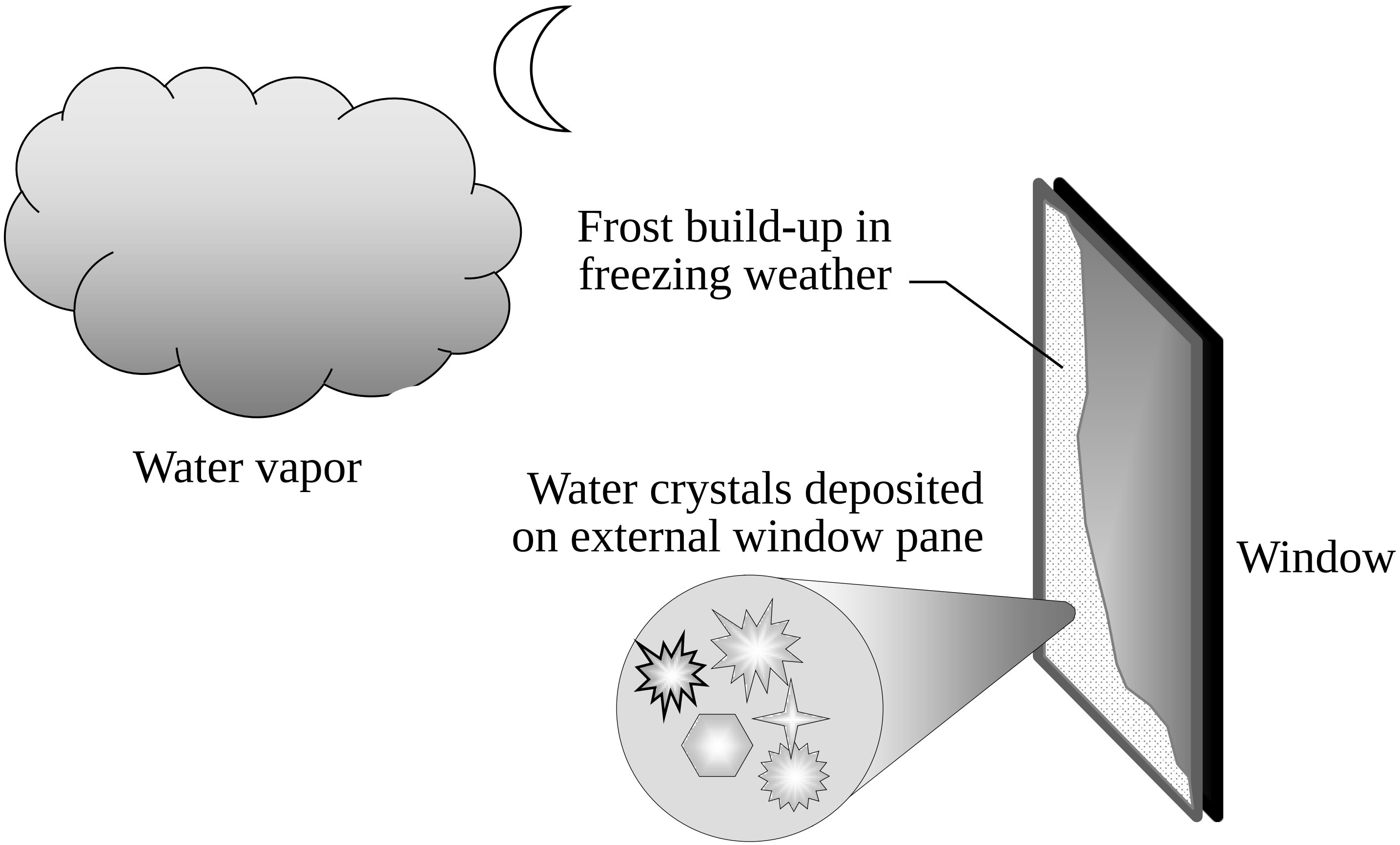


Figure 5.8

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Density of Objects

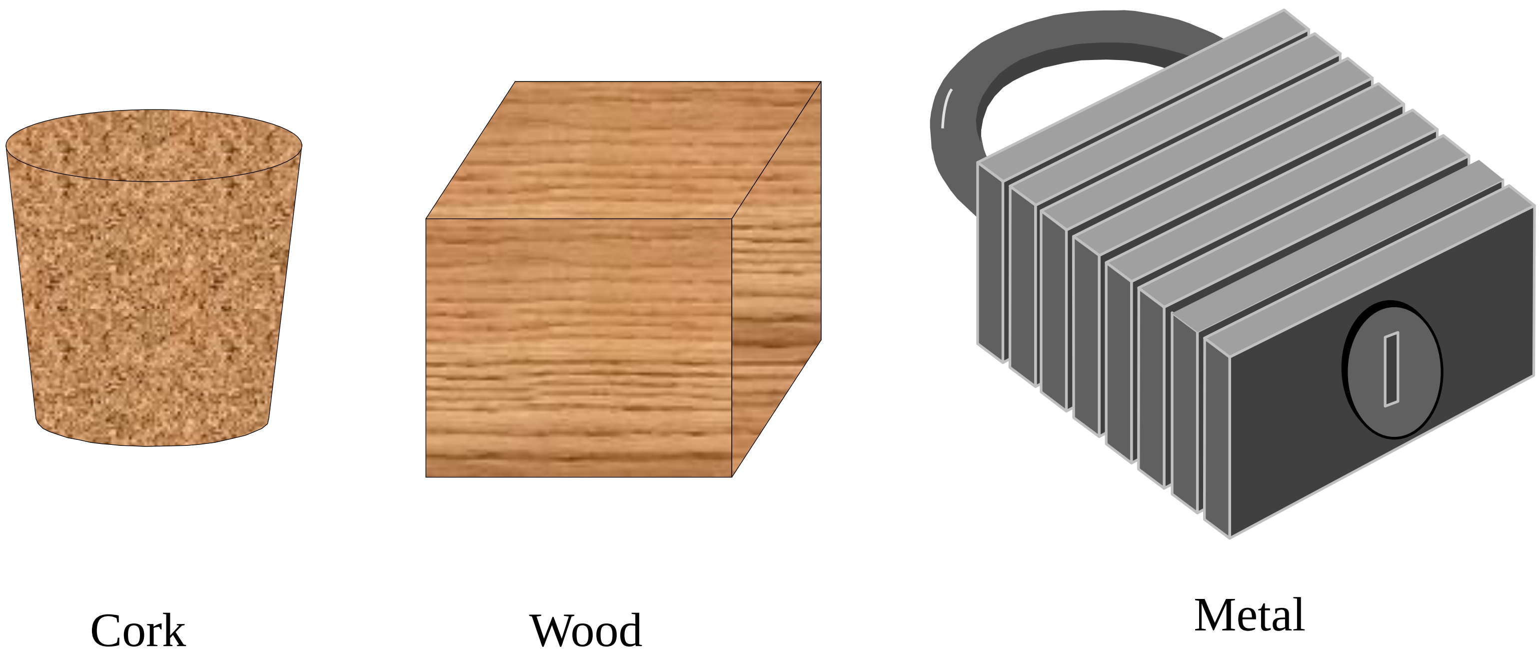


Figure 5.9

Densities of Some Common Substances

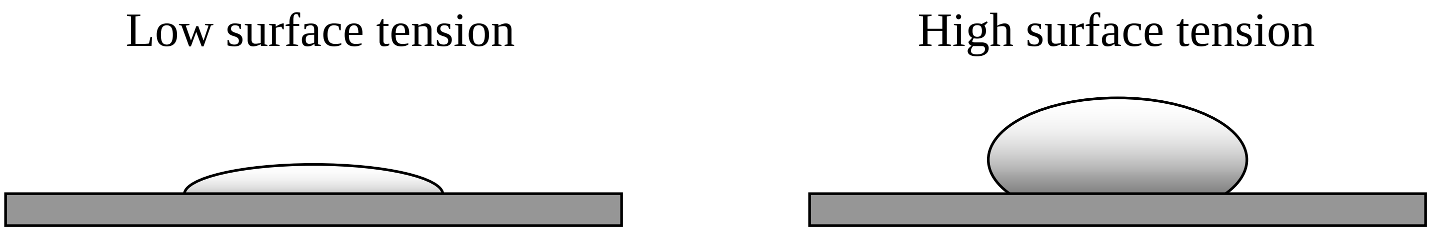
Substance	Physical State	Density (g/cm^3)
Hydrogen	Gas	0.000089
Oxygen	Gas	0.0014
Water	Liquid	1.0
Table Salt	Solid	2.16
Silicon	Solid	2.33
Aluminum	Solid	2.70
Gold	Solid	19.3

Table 5.2

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Surface Tension of a Liquid on a Wafer



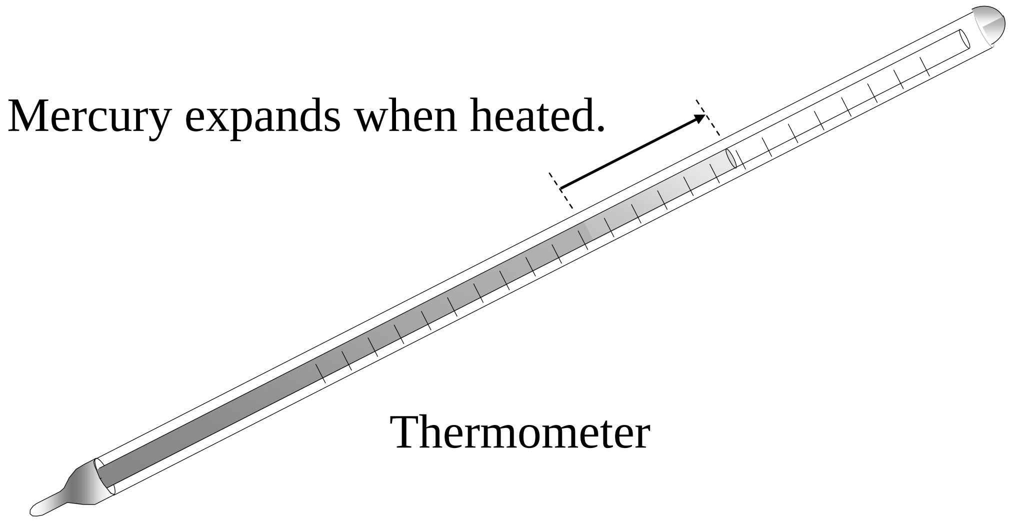
HF-dip to etch SiO_2 on Si

Figure 5.10

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

Thermal Expansion of a Heated Object



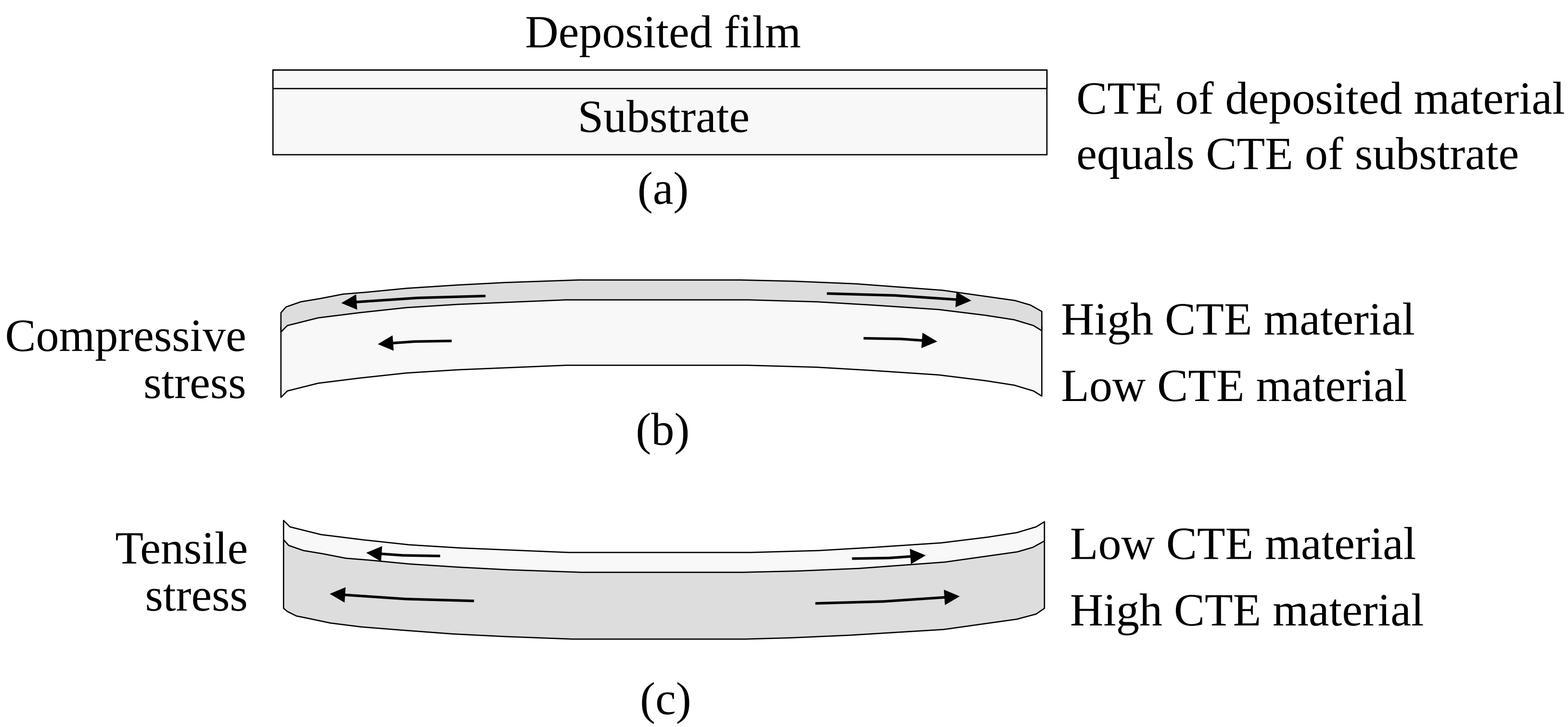
The amount a material expands due to heating is known as its **coefficient of thermal expansion**

Figure 5.11

Properties of Materials

- Temperature
- Pressure and Vacuum
- Condensation
- Vapor Pressure
- Sublimation and Deposition
- Density
- Surface Tension
- Thermal Expansion
- Stress

CTE Mismatch of Two Materials



- The reliability of a chip is improved by ensuring materials have minimal stress.

Figure 5.12

Process Chemicals

Chemicals are used in SMT to:

- **Clean** or prepare the wafer surface with wet chemical solutions and ultrapure water rinse.
- **Dope** the wafer with energetic atoms to create p-type and n-type silicon.
- **Deposit** the different metal conductor layers with the necessary dielectric layers between the conductors.
- **Grow** the thin silicon dioxide film to be used as the critical MOS gate dielectric.
- **Etch** thin films with plasma or wet chemicals to selectively remove material and form the required pattern in the film.

Process Chemicals

Liquids (ppb)

- Acids (H_3O^+)
- Bases (OH^-)
- pH
- Solvents
- Chemical Distribution

Common Acids Used in Semiconductor Manufacturing

Acid	Symbol	Examples of Use*
Hydrofluoric acid	HF	Etching of silicon dioxide (SiO_2) and to clean quartzware.
Hydrochloric acid	HCl	Wet cleaning chemical that is part of the standard clean 2 (SC-2) solution to remove heavy metals from wafer.
Sulfuric acid	H_2SO_4	Solution known as "Piranha" (7 parts H_2SO_4 to 3 parts of 30% hydrogen peroxide (H_2O_2)) used to clean wafers.
Buffered oxide etch (BOE): Solution of hydrofluoric acid and ammonium fluoride	HF and NH_4F	Etching of silicon dioxide (SiO_2) film.
Phosphoric acid	H_3PO_4	Etching of silicon nitride (Si_3N_4)
Nitric acid	HNO_3	Used in mixture of HF and HNO_3 to etch phosphosilicate glass (PSG).
Boron Tribromide	BBr_3	Liquid source of boron dopant.
Phosphorus Oxychloride	$POCl_3$	Liquid source of phosphorus dopant.

Table 5.3

Common Bases Used in Semiconductor Manufacturing

Base	Symbol	Example of Use
Hydrogen peroxide	H_2O_2	Catalyst in etch solution
Ammonium hydroxide	NH_4OH	Cleaning solution
Potassium hydroxide	KOH	Positive photoresist developer
Tetramethyl ammonium Hydroxide	TMAH	Positive photoresist developer

Table 5.4

The pH Scale for Different Chemicals

pH	Household Chemicals	
1	Car battery acid (sulfuric acid, H_2SO_4)	Corrosive
2		
3	Lemon juice, vinegar	
4	Soda, wine	
5	Tomato juice, beer	
6	Urine	
7	Tap water, milk, saliva	
8	Blood, saliva	
9	Milk of magnesia	
10	Detergents	
11	Household ammonia	
12		
13	Household drain cleaners	Caustic
14	Nickle-cadmium battery (NaOH base)	

Figure 5.13

Common Solvents Used in Semiconductor Manufacturing

A solvent is a substance capable of dissolving another substance to form a solution.

Solvent	Common Name	Example of Use
Deionized Water	DI Water	Widely used to rinse wafers.
Isopropyl alcohol	IPA	General purpose cleaning solvent.
Trichloroethylene	TCE	Solvent used for wafer and general cleaning.
Acetone	Acetone	General purpose cleaning solvent (stronger than IPA).
Xylene	Xylene	Strong cleaning solvent, may also be used for photoresist edge bead removal.

Table 5.5

Bulk Chemical Distribution

Use for : safe, high-quality, uninterrupted delivery of chemicals from storage vessel to process tools is critical

Photo courtesy of Advanced Micro Devices

Bulk Chemical Distribution vs. point-of use (PR)

point-of use:
少量或儲存
時間短如光阻

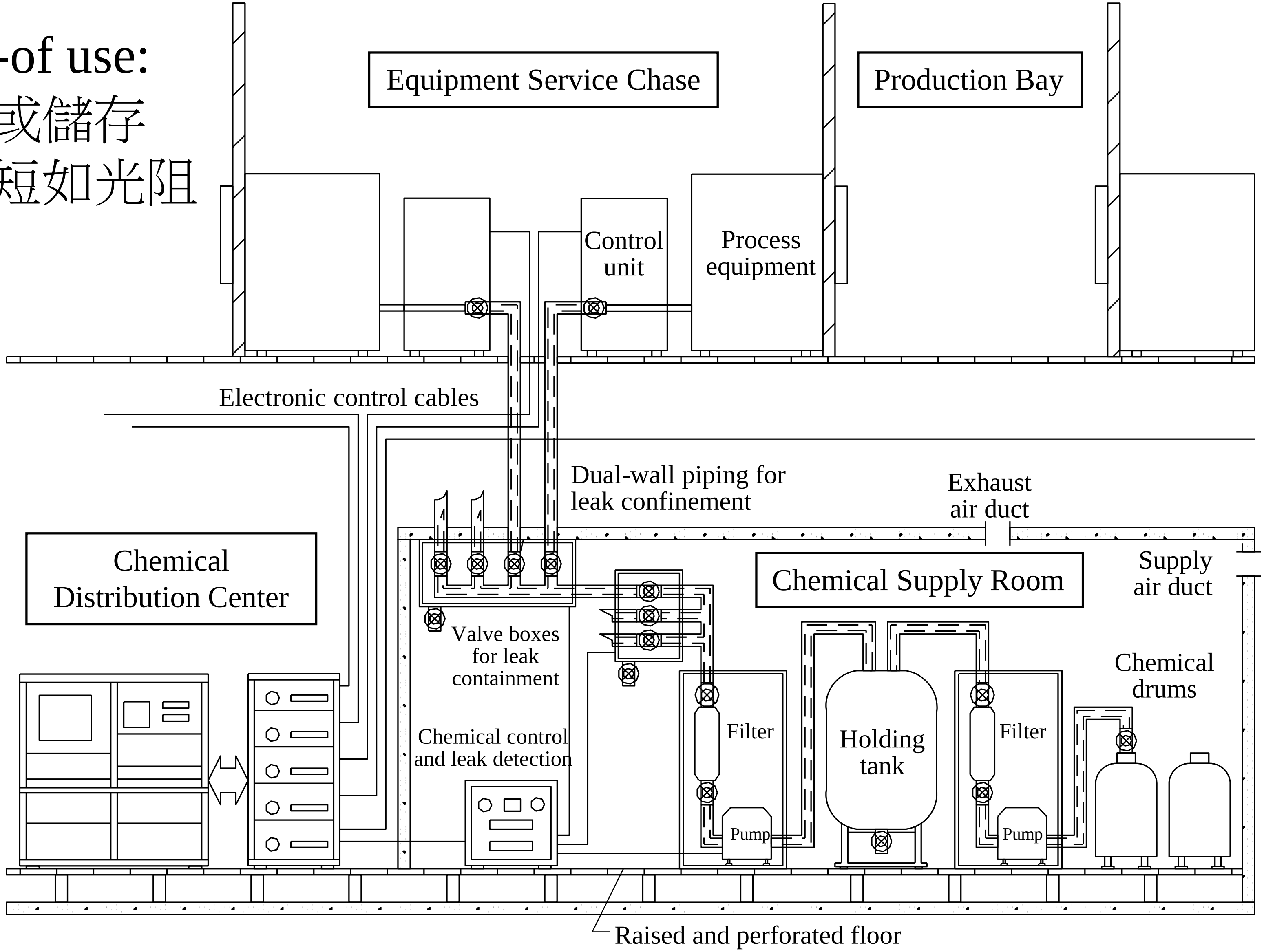


Figure 5.14

Process Chemicals

Gases (~ 50 gases)

- Bulk Gases (99.99999%)
- Specialty Gases (99.99%)
  - Gas purge
  - Gas piping
  - Gas line connections
  - Gas stick
  - Cylinder change-out
- Classifying Specialty Gases
  - toxic, corrosive, reactive, and pyrophoric

Bulk Gases

Type of Gas	Gas	Symbol	Example of Use
Inert	Nitrogen	N_2	Purge gas lines and process chambers of moisture and residual gas.
	Argon	Ar	Gas used in process chambers during processing.
	Helium	He	Gas used in process chambers and also to leak check vacuum chambers.
Reducing	Hydrogen	H_2	Carrier gas for epitaxial layer process.
Oxidizing	Oxygen	O_2	Process chamber gas.

Table 5.6

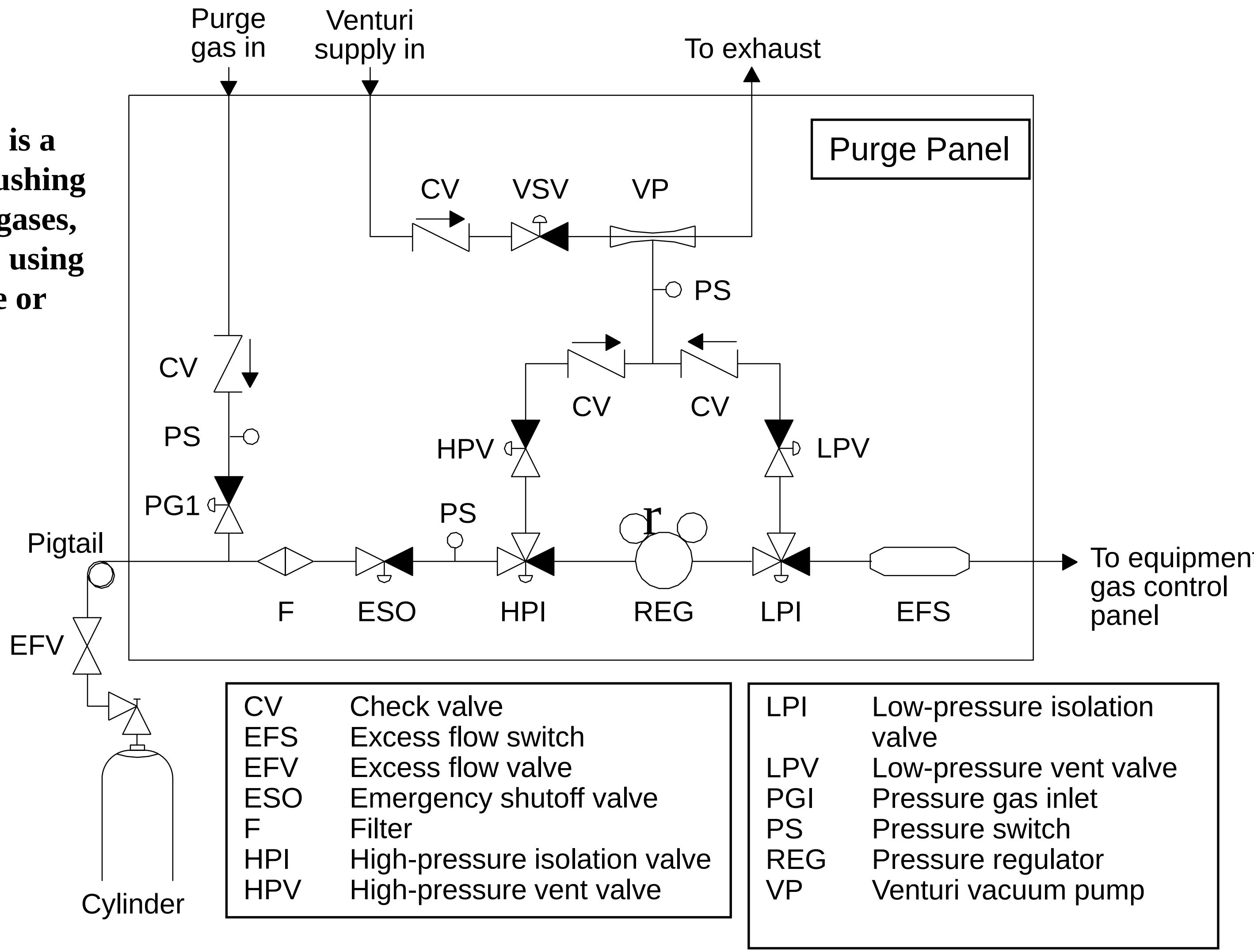
Bulk Gas Distribution System

1. In large storage tanks or 1000-lb bulk tube trailer.
2. Benefits: reliable, less particulate contamination, and less human involvement in the daily delivery of the gas.

Photo 5.2

Typical Specialty Gas System Design

•A **gas purge** **is a method of flushing undesirable gases, air, or water, using N2 gas purge or vacuum**



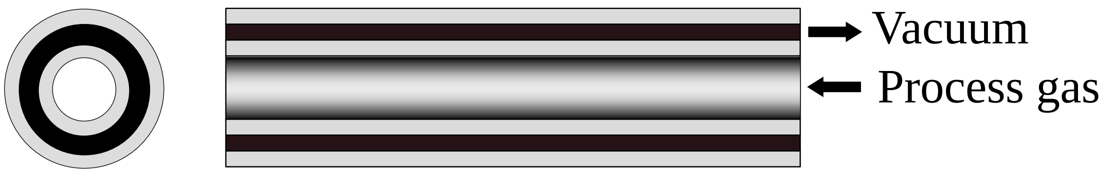
Used with permission from International SEMATECH

Figure 5.15

Double-Walled Tubing

Electropolishing: wet etch (30 μm) to reduce contaminants, and coating a Cr to reduce emitting particle

Double-walled tubing



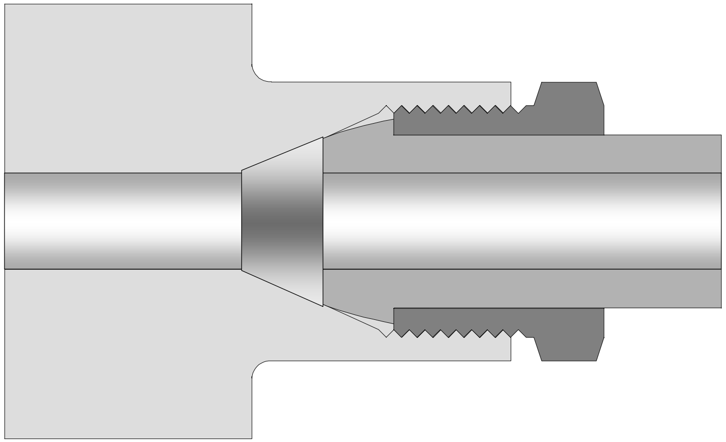
Used with permission from International SEMATECH

- Piping is constructed with electropolished 316L stainless steel tube.
- No plastic part is used in piping, except some membrane gas filters.

Figure 5.16

CGA Gas Line Connector

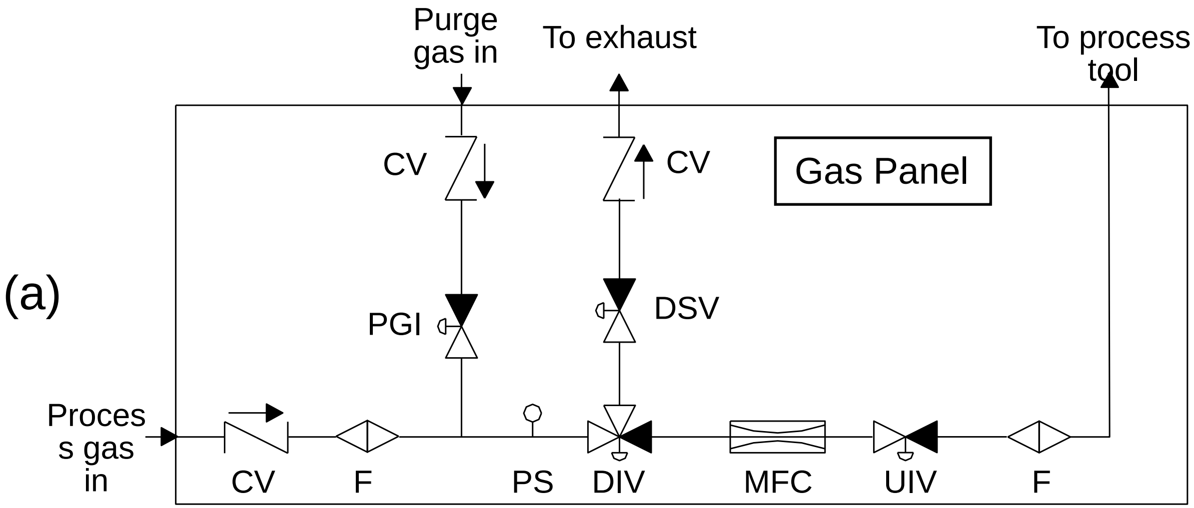
CGA: compressed gas association



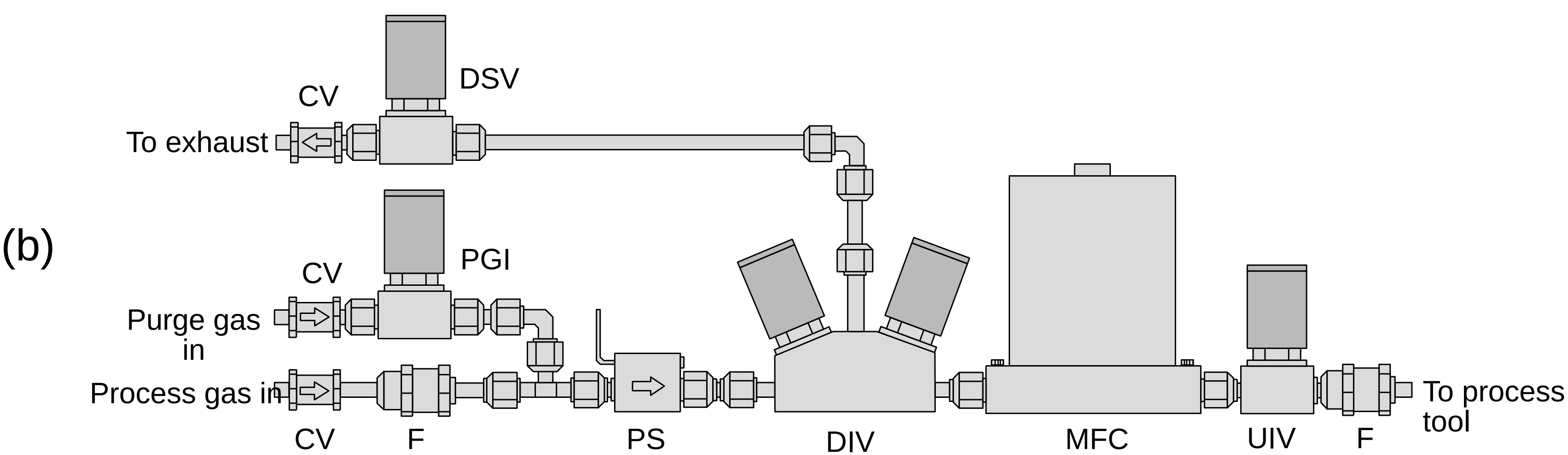
Used with permission from International SEMATECH

Figure 5.17

Gas Stick at Process Tool



CV	Check valve
DIV	Downstream isolation valve
DSV	Downstream vent valve
F	Filter
MFC	Mass flow controller
PGI	Purge gas inlet valve
PS	Pressure switch
UIV	Upstream isolation valve



(a) Schematic used with permission from International SEMATECH, (b) Component diagram based on Swagelok components, Swagelok Co. Catalog provided by Arthur Valve & Fitting Co., Austin, TX.

Figure 5.18

Specialty Gas Cylinder

Cylinder change-out

- incorrectly purging gas lines causes contamination
- fall over
- using tube trailer to reduce times of change-out

Photo courtesy of Praxair Technology, Inc.

Photo 5.3

Some Common Specialty Gases

Class of Gas	Gas	Symbol	Example of Use
Hydrides	Silane	SiH_4	Source of silicon in process chamber
	Arsine	AsH_3	Source for n-type doping of epitaxial films (diluted with hydrogen to better control process)
	Phosphine	PH_3	Source of phosphorous for n-type wafer doping (diluted with hydrogen)
	Diborane	B_2H_6	Source of boron for p-type wafer doping (diluted with hydrogen)
	Tetraethyl Orthosilicate (TEOS)	$Si(OC_2H_5)$	Source of silicon dioxide
	Silicon tetrachloride (also tetrachlorosilane)	$SiCl_4$	Growth of epitaxial silicon
	dichlorosilane (DCS)	SiH_2Cl_2	Growth of epitaxial silicon
Fluorinated Compounds	Nitrogen trifluoride	NF_3	Process chamber gas as source of flouride ions
	Tungsten hexafluoride	WF_6	Process gas
	Tetrafluoromethane)	C_2F_4	Process gas
	Carbon tetrafluoride	CF_4	Process gas
	Silicon tetrafluoride	SiF_4	Process gas
	Chlorine trifluoride	ClF_3	Process chamber cleaning gas
Acid Gases	Boron triflouride	BF_3	Wafer doping gas
	Chlorine	Cl_2	Process gas
	Boron trichloride	BCl_3	Process and doping gas
	Hydrogen chloride	HCl	Process gas
Other Gases	Ammonia	NH_3	Process gas
	Nitrous oxide	N_2O	Process gas (source of nitrogen)