Figure 7.38: The main gate at Auschwitz, through which an estimated two million victims of Nazi genocide passed.

Despite the horror associated with the use of hydrogen cyanide for the Holocaust, it was used by 11 US states for the death penalty (Figure 7.39). Arizona, Maryland, and Missouri retain the gas chamber as a secondary method of execution though they have lethal injection as the primary method. Potassium cyanide (KCN) pellets are placed into a compartment directly below the chair in the gas chamber (Figure 7.39). The condemned person is then strapped into the chair, and the airtight chamber sealed. Concentrated sulfuric acid (H_2SO_4) is then poured down a tube onto the cyanide pellets to generate hydrogen cyanide, (7.22). Execution by gas chamber is especially unpleasant for the witnesses to the execution due to the physical responses exhibited during the process of dying, including: convulsions and excessive drooling.

Figure 7.39: The former gas chamber in San Quentin State Prison, now an execution chamber for lethal injection, in which the State of California executed 192 men and 4 women.

7.2.3.4 Bibliography

- J. Wu and N. J. Evans, *Astrophys. J.*, 2003, **592**, L79.

7.2.4 Oxides of Carbon

7.2.4.1 Carbon Monoxide[6]

Carbon monoxide (CO) is iso-electronic with nitrogen (N_2) and formed through the incomplete combustion of carbon, (7.25), or hydrocarbon compounds.

$$2\,C + O_2 \rightarrow 2\,CO \tag{7.25}$$

Carbon monoxide may also be made from steam and coal as part of synthesis gas, (7.27). A convenient laboratory preparation of CO is the dehydration of formic acid by sulfuric acid, (7.26).

$$C + H_2O \rightarrow CO + H_2 \tag{7.26}$$

$$HCO_2H \rightarrow CO + H_2O \tag{7.27}$$

---

[6] This content is available online at <http://cnx.org/content/m32939/1.2/>.

7.2.4.1.1 Hazards and toxicity

Carbon monoxide is flammable, (7.28), and has an explosive limit of 12.5 – 74% with an auto ignition temperature of 609 °C.

$$2\,CO + O_2 \rightarrow 2\,CO_2 \qquad (7.28)$$

Carbon monoxide is also very toxic; however, it is colorless, odorless, tasteless and non-irritating all of which increase its danger. The incomplete combustion of hydrocarbon (natural gas or heating oil) or carbon sources (coal or charcoal) is a common hazard in the home. In a closed environment (e.g., charcoal grill in room with no, or poor, ventilation) as carbon uses up oxygen in room the formation of toxic carbon monoxide results instead of carbon dioxide (CO_2).Typical sources of CO in the home are shown in Figure 7.40.

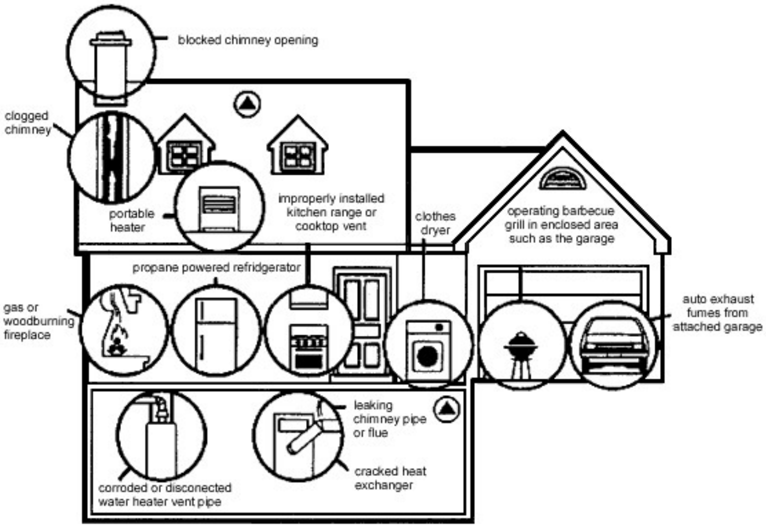


Figure 7.40: Potential sources of carbon in the home. Copyright: Fire Safety Council.

The toxicity of CO is due to its competition with oxygen at the heme binding site in hemoglobin. The binding affinity for CO is 200 times greater than that for oxygen, meaning that just small amounts of CO dramatically reduces hemoglobin's ability to transport oxygen around the body. The bright red color of the CO-heme complex is the reason that chronic exposure results in the skin adopting a bright red color. The symptoms of CO poisoning include headache, nausea, weakness, and eventually death. When air contains CO levels as low as 0.02%, headache and nausea occur; if the CO concentration is increased to 0.1%, unconsciousness will follow.

> NOTE: Cigarette smoke containing large amounts of carbon monoxide and as a result heavy smokers can have up to 20% of the oxygen-active sites in their blood blocked by CO. However, despite this hazard, cigarettes would be even more deadly if they were not burnt. A key (and often engineered) ingredient in cigarettes is the addictive drug nicotine. Nicotine is an alkaloid (Figure 7.41a) as is caffeine (Figure 7.41b) that is in coffee and tea. The lethal dose of caffeine is approximately 10 g, which relates to approximately 70 – 100 cups of coffee (assuming a concentration of 100- 150 mg per cup). Alternatively, a lethal dose of caffeine from cola would require approximately 180 – 280 12 oz bottles, each containing 35 – 44 mg. In comparison nicotine has a lethal dose of 50 mg.

This means that 12 cigarettes can provide a lethal does if consumed. The only reason smoking 12 cigarettes do not kill immediately is that the majority of the nicotine is burnt in the smoking of the cigarette. If this were not true smokers would be killed before they could develop a habit!

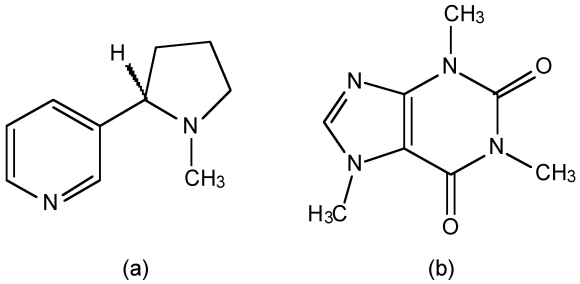


Figure 7.41: The molecular structures of (a) nicotine and (b) caffeine.

7.2.4.1.2 Structure and bonding

The bonding in CO involves 1 σ-bond and 2 sets of π-bonds (Figure 7.42). The C-O bond distance in carbon monoxide is 1.1 Å and therefore consistent with a triple bond. In comparison a typical C-O single bond is *ca.* 1.43 Å, and an average C-O double bond is *ca.* 1.23 Å. The major absorption band in the infra red spectrum for CO is 2143 cm^{-1}, while for ^{13}CO it is 2099.2 cm^{-1}.

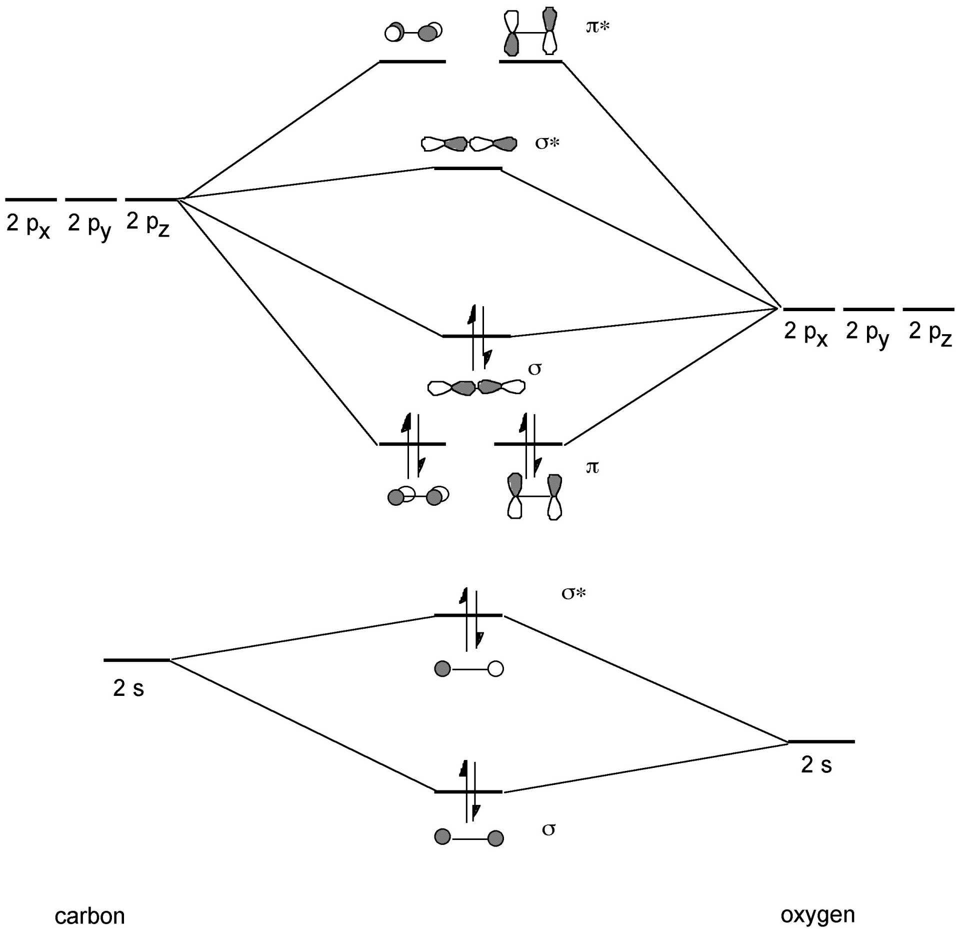


Figure 7.42: The carbon monoxide molecular orbital diagram.

7.2.4.2 Carbon Dioxide[7]

Carbon dioxide (CO_2) is the most stable oxide of carbon and is formed from the burning of carbon or carbon containing compounds in air or an excess of oxygen, (7.29). For industrial applications it is usually prepared from the decomposition of calcium carbonate (limestone), (7.30), rather than separation from combustion products.

$$C + O_2 \rightarrow CO_2 \quad (7.29)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (7.30)$$

---

[7] This content is available online at <http://cnx.org/content/m32935/1.2/>.

7.2.4.2.1 Phase chemistry of carbon dioxide

Carbon dioxide does not exists as a liquid under normal atmospheric pressure, but solid CO_2 (also known as *dry ice*) sublimes at -78.5 °C (Figure 7.43). Dry ice (Figure 7.44) is commonly used as a refrigerant for food or biological sample preservation.

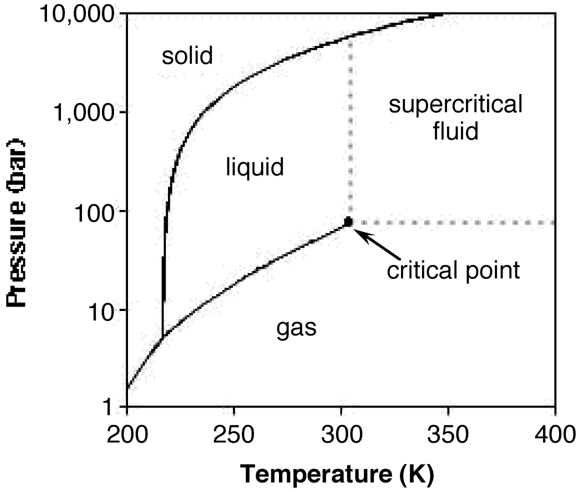


Figure 7.43: The phase diagram for carbon dioxide.

Figure 7.44: Photograph of a solid block of *dry ice*.

NOTE: When dry ice is placed in water (especially heated) sublimation is accelerated, and a low-sinking dense cloud of fog (smoke-like) is created. This is used in fog machines, at theaters, concerts, haunted houses, and nightclubs for dramatic effects (Figure 7.45). Fog from dry ice hovers above the ground unlike other artificial fog machines (that use partial combustion of oil) where the fog rises like smoke.

Figure 7.45: Dry ice generated smoke being used during Iron Maiden's *Somewhere Back in Time World Tour*. Copyright: Pyrotek.

7.2.4.2.1.1 Supercritical carbon dioxide

As noted above carbon dioxide usually behaves as a gas in air at standard temperature and pressure (STP = 25 °C and 1 atm) or as a solid when frozen. However, if the temperature and pressure are both increased from STP to be at or above the critical point (Figure 7.43), carbon dioxide adopts properties midway between a gas and a liquid ($T_c = 31.1$ °C and $P_c = 72.9$ atm).

Supercritical CO_2 has become an important industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. In this regard it is seen as a promising green solvent. One of the biggest applications is the decaffeination of coffee and tea without leaving any residue and allowing the caffeine to be separated and used in other beverage products.

7.2.4.2.2 Structure and bonding

Carbon dioxide is a linear molecule due to π-localization. The bonding in CO_2 involves 2 σ-bond and 2 sets of 3 center π-bonds (Figure 7.46). The C-O bond length of 1.2 Å should be compared to the value observed for organic carbonyls (e.g., ketones, esters, aldehydes) of 1.2 – 1.3 Å.

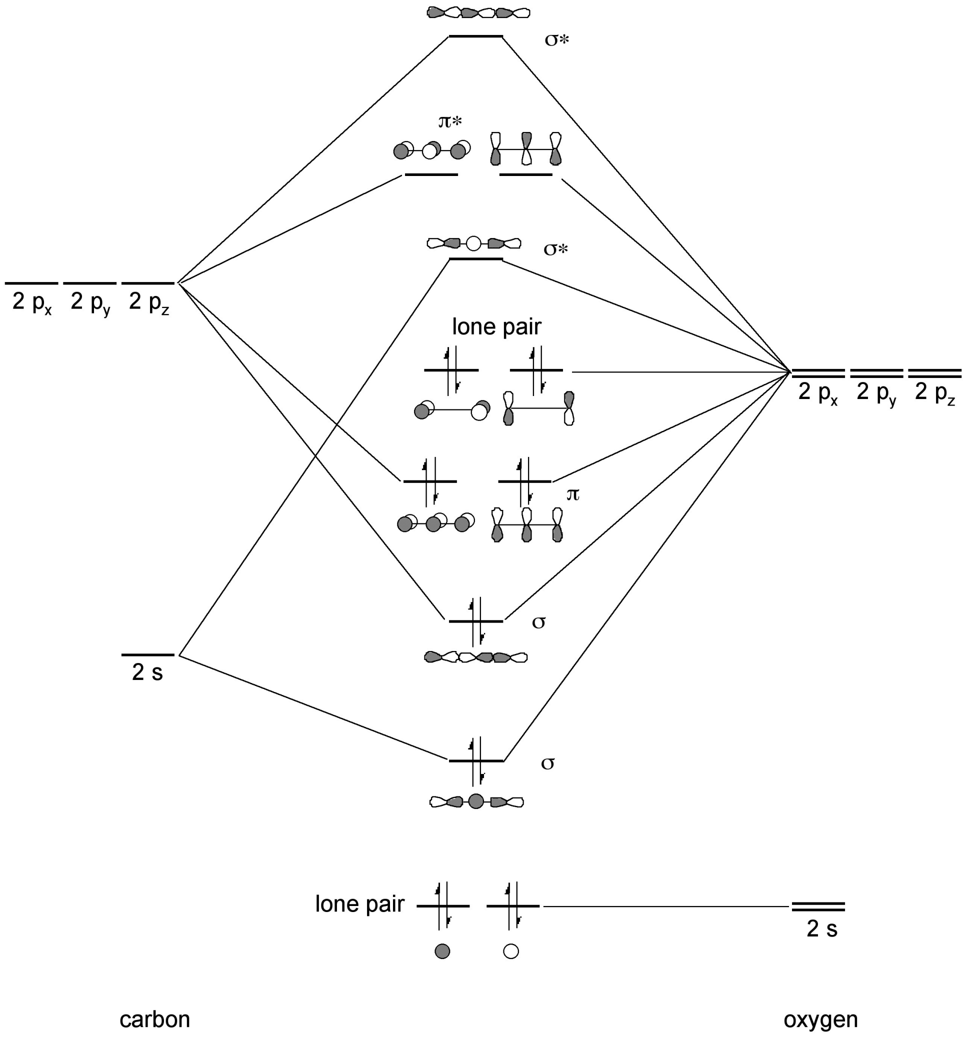


Figure 7.46: The carbon dioxide molecular orbital diagram.

7.2.4.2.3 Dissolution and reaction with water

Although CO_2 has no dipole moment it is very polar (dielectric constant = 1.60 at 0 °C, 50 atm) and consequently dissolves in polar solvents such as water up to a concentration of 0.18% (0.04 M). Most of it (+99%) is present as solvated CO_2 (Figure 7.47), and only ca. 0.2% is reacted to form carbonic acid, (7.31), with subsequent equilibria resulting in the formation of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}).

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (7.31)$$

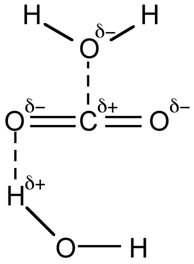


Figure 7.47: Typical water solvation of carbon dioxide.

The overall reaction involves a series of equilibria. The first equilibrium is the formation of carbonic acid, (7.32). The reaction rates, (7.33), are on the magnitude of 1 second (i.e., slow), and as a consequence when carbon dioxide is carried in the body an enzyme is present to speed up the reaction.

$$CO_{2(solv)} + H_2O \underset{k_{H_2CO_3}}{\overset{k_{CO_2}}{\rightleftharpoons}} H_2CO_3 \tag{7.32}$$

$$K = \frac{k_{H_2CO_3}}{k_{CO_2}} = \frac{25}{0.04} = 600 \tag{7.33}$$

The 2nd equilibrium is as a consequence of first ionization of carbonic acid to form bicarbonate (HCO_3^-), (7.34). In contrast to the first reaction, (7.32), this reaction is very fast with a $K_{eq} = 1.6 \times 10^{-4}$ @ 25 °C.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \tag{7.34}$$

The 3rd equilibrium involves the formation of the carbonate ion(7.35), and has a $K_{eq} = 4.84 \times 10^{-11}$. Carbonate ($CO_3^{2-}$) is a delocalized ligand, which can act as a mono or bidentate or bridging group.

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{7.35}$$

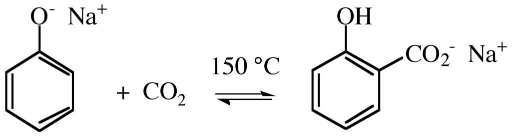
The formation of carbonic acid is the reason that even in the absence of pollutants (such as SO_2) natural rain water is slightly acidic due to dissolved CO_2. The equilibrium associated with carbonic acid is also responsible for the buffering of the pH in blood.

7.2.4.2.4 Reaction chemistry

Photosynthesis in plants reduces CO_2 to organic matter but similar reactions have yet to be developed in non-living systems.

Grignards react readily with carbon dioxide to form the carboxylate, which yields the associated carboxylic acid upon hydrolysis, (7.36). Similar reactions occur with other organometallic compounds. In addition, CO_2 reacts with alkali metal salts of phenols (phenolates) to yield the hydroxy-carboxylate, (7.37).

$$RMgX + CO_2 \rightarrow RCO_2MgX \xrightarrow{H_2O} RCO_2H + HOMgX \tag{7.36}$$



(7.37)

A number of complexes of CO_2 with transition metals are known in which the coordination can occur via the central carbon (Figure 7.48a) or the C=O bond (Figure 7.48b). Alternatively, CO_2 can bridge two metal centers.

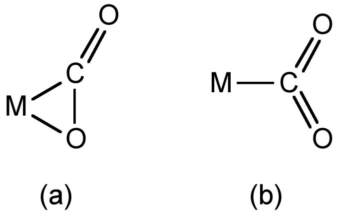


Figure 7.48: Bonding modes of CO_2 to transition metals.

7.2.4.2.5 Global warming and carbon dioxide

Global warming is the process of the observed increase in the average temperature of the Earth's near-surface air and oceans since the mid-20th century. Global surface temperature increased 0.74 °C (1.33 °F) between the start and the end of the 20th century (Figure 7.49). It is generally agreed that the majority of this temperature increase has occurred since the middle of the 20th century and was caused by increasing concentrations of greenhouse gases resulting from burning fossil fuels (the generation of additional CO_2) and deforestation (the loss of a mechanism for the consumption of CO_2), see Figure 7.49. While it is appreciated that natural phenomena (including solar radiation and volcanoes) produced most of the warming from pre-industrial times, the magnitude of the changes brought on by global industrialization is more significant.

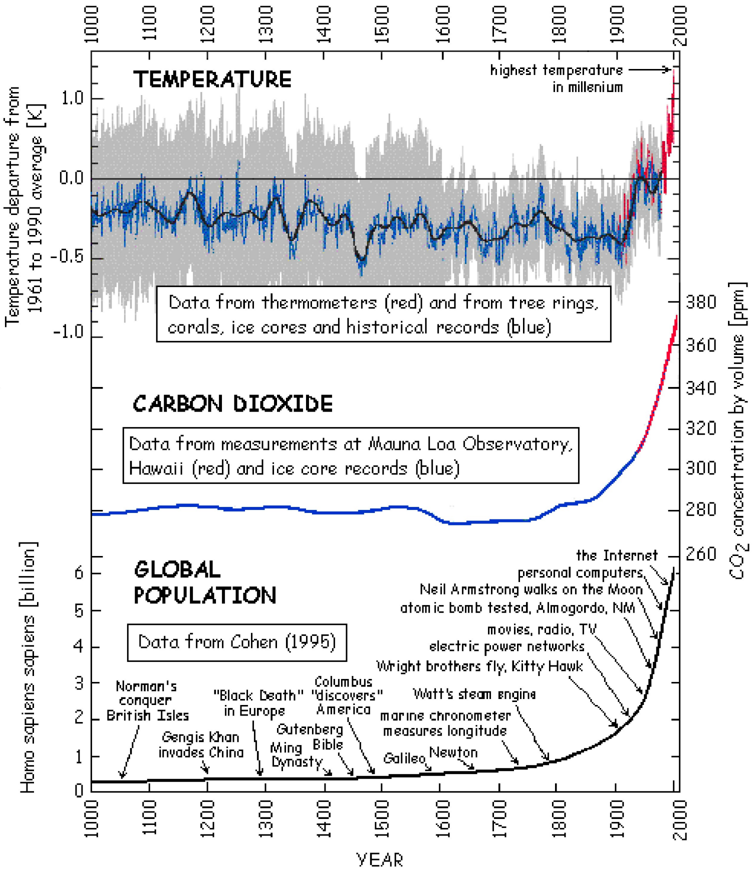


Figure 7.49: Correlation of Earth average temperature with carbon dioxide and global population.

The Earth's atmosphere has two functions. First, the ozone (O_3) in the upper atmosphere screens harmful UV from reaching the surface of the Earth. Second, as solar radiation penetrates the atmosphere a portion of the heat is then retained as a consequence of the CO_2 in the atmosphere. It is this process that modulates the surface temperature and provides a stable environment for life. The failure or alteration of either of these processes can have a dramatic effect on the livability of a planet.

Consider the relative position of Venus, Earth, and Mars to the Sun (Figure 7.50). The closer a planet is to the sun the greater the UV radiation and the greater the heating of the planet; however, the temperature is also greatly modulated by the atmosphere. Venus has an atmosphere comprising 95% CO_2 and has a surface temperature of approximately 450 °C. In contrast, while Mars' atmosphere is also 95% CO_2, it is only 1% as dense as that of Earth's, and thus the surface temperatures range from 40 °C during the day (due to radiative heating) to –80 °C at night (due to the lack of retained heat because of the thin atmosphere). These should be compared to Earth's atmosphere which is 0.038% CO_2, which allows for the correct amount of heat to be retained to sustain life. Clearly any significant change in the CO_2 content of the atmosphere will change the global temperatures of a planet.

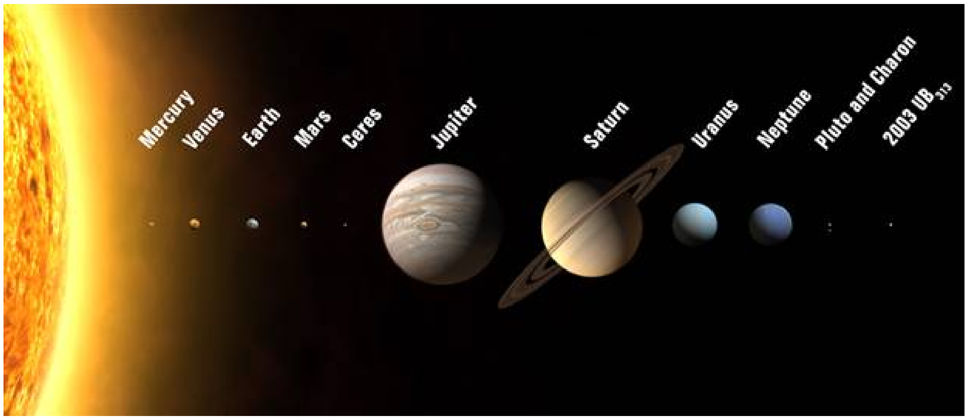


Figure 7.50: The relative size and position of the planets from the sun.

7.2.4.2.6 Bibliography

- N. Stern, *The Stern Review: The Economics of Climate Change*, HM Treasury, London.
- R. B. Gupta and J.-J. Shim, *Solubility in Supercritical Carbon Dioxide*, CRC Press (2006).
- *Carbon Dioxide Capture and Storage: Special Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press (2005).

7.2.4.3 Suboxides of Carbon[8]

7.2.4.3.1 Carbon suboxide

Carbon suboxide is the third oxide of carbon, C_3O_2. It is made from the dehydration of malonic acid, (7.38), with P_4O_{10} above 140 °C Like carbon dioxide, the C_3O_2 molecule is linear, with pπ-pπ bonding.

$$CH_2(CO_2H)_2 \rightarrow O{=}C{=}C{=}C{=}O + 2\,H_2O \tag{7.38}$$

Gaseous carbon suboxide has an evil smell and while stable at –78 °C it polymerizes at 25 °C. Photolysis of C_3O_2 yields the unstable C_2O. As expected from its synthesis, carbon suboxide reacts slowly with water to form malonic acid, i.e., the reverse of (7.38); however, the reaction with stronger nuceophiles such as amines is rapid, (7.39).

$$C_3O_2 + 2\,HNR_2 \rightarrow R_2NC(O)CH_2C(O)NR_2 \tag{7.39}$$

7.2.4.3.2 Mellitic acid anhydride

The anhydride of mellitic acid (Figure 7.51a) may be considered as an oxide of carbon since its chemical formula contains only carbon and oxygen, i.e., $C_{12}O_9$ (Figure 7.51b).

---

[8] This content is available online at <http://cnx.org/content/m32934/1.2/>.

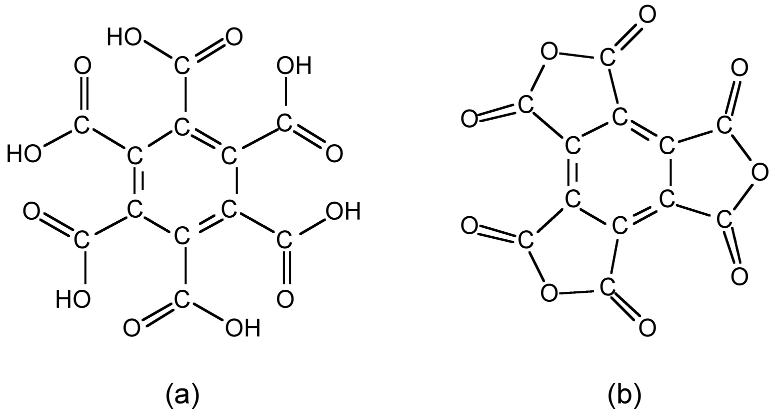


Figure 7.51: Structures of (a) mellitic acid and (b) its anhydride.

7.2.5 Carbon Halides[9]

There are two general classes of carbon halides.

1. Homoleptic halides, e.g., CCl_4, CCl_2F_2, C_6Cl_6, etc.
2. Carbonyl halides, e.g., $Cl_2C{=}O$.

A summary of some simple carbon halides is given in Table 7.8.

Compound	**Mp (°C)**	**Bp (°C)**	**Remarks**
CF_4	-185	-128	Very stable gas
CCl_4	-23	76	Colorless liquid, stable
CBr_4	93	190	Pale yellow solid, decomposes upon boiling
CI_4	171	-	Bright red solid, decomposes prior to boiling, sublimed at low pressure
$F_2C{=}O$	-114	-83	Decomposed by H_2O
$Cl_2C{=}O$	-118	8	Phosgene, highly toxic

continued on next page

---

[9] This content is available online at <http://cnx.org/content/m32944/1.4/>.

$Br_2C{=}O$	-	65	Fumes in air

Table 7.8: Physical properties of simple halogen compounds of carbon.

7.2.5.1 Carbon tetrahalides

The carbon tetrahalides are generally prepared by the direct (thermal) reaction of carbon with the appropriate halogen, (7.40); however, specific syntheses are possible for each derivative.

$$C + 2\,X_2 \rightarrow CX_4 \tag{7.40}$$

In addition to the direct reaction of fluorine with carbon, CF_4 can be prepared from SiC, (7.41). The SiF_4 side product is removed by passing the reaction mixture through NaOH solution, in which SiF_4 reacts to form silicate. The difference in reactivity of SiF_4 and CF_4 is attributable to the lack of an energetically accessible five-coordinate intermediate required for the associative mechanism.

$$SiC + F_2 \rightarrow SiF_4 + CF_4 \tag{7.41}$$

Carbon tetrabromide can be obtained by bromination of CH_4 with HBr or Br_2, or by the reaction of CCl_4 with $AlBr_3$, (7.42). Carbon tetraiodide (CI4) can be made by the Lewis acid catalyzed halogen exchange reaction, (7.43).

$$3\,CCl_4 + 4\,AlBr_3 \rightarrow 3\,CBr_4 + 4\,AlCl_3 \tag{7.42}$$

$$CCl_4 + 4\,C_2H_5I \rightarrow CI_4 + 4\,C_2H_5Cl \tag{7.43}$$

CF_4 is very stable. In fact, it is so stable that it does not even react with molten sodium. In contrast to CF_4, carbon tetrachloride (CCl_4) reacts readily with alkali metals (K and Na) or other strong reducing agents (e.g., F_2, Al, Ba, Be, and Zn). While CCl_4 is thermodynamically unstable with respect to hydrolysis, it is kinetically stable, and thus finds extensive use as a solvent. Photolysis can result in the transfer of a chloride radical to various substrates. It is also used in the conversion of metal oxides to the chlorides. Carbon tetrabromide (CBr_4) is insoluble in water and other polar solvents, but soluble in benzene. Carbon tetraiodide (CI_4) decomposes thermally, (7.44).

$$2\,CI_4 \rightarrow 2\,I_2 + I_2C{=}CI_2 \tag{7.44}$$

The decreasing stability of CX_4, from fluorine to iodine, is directly related to the C-X bond energy (Table 7.9).

C-X	**Bond energy (kJ/mol)**
C-F	485
C-Cl	327
C-Br	285
C-I	213

Table 7.9: Bond energies for carbon-halide bonds.

7.2.5.1.1 Hazards

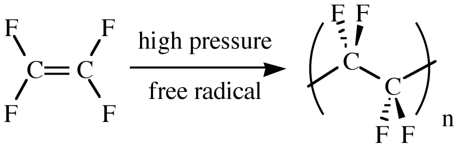
Despite its use as a solvent CCl_4 has significant hazardous effects. Inhalation of carbon tetrachloride vapor can cause headaches, mental confusion, depression, fatigue, loss of appetite, nausea, vomiting, and coma. The symptoms can take many hours to appear. The vapor and liquid irritate the eyes, and internal irritation, nausea, and vomiting are caused when taken orally. Chronic effects from prolonged inhalation include bronchitis and jaundice, while skin exposure can cause dermatitis.

Carbon tetrabromide is toxic by inhalation, and the vapor is narcotic if taken in high concentrations. As with CCl_4, CBr_4 can react explosively with alkali metals.

7.2.5.2 Higher homoleptic halides

Organic compounds that contain only carbon and a halogen are called halocarbons, and these include fluorocarbons and chlorocarbons. The easiest route to fluorocarbons involves the reaction of a hydrocarbon with a high valent fluoride (e.g., CoF_3) or the reaction of a chlorocarbon with SbF_3. In general, chlorocarbons with sp^3 carbon atoms are more stable than those with sp^2 carbon centers. The exception to this is aromatic compounds such as C_6Cl_6.

The physical properties of fluorocarbons range from inert to toxic. Thus, poly(tetrafluoroethylene), $(C_2F_4)_n$, known by either its acronym (PTFE) or its trade name (Teflon), is chemically inert and has a low coefficient of friction (Table 7.10). As a consequence its uses include coatings on armor-piercing bullets (to stop the wear on the gun barrel), laboratory containers and magnetic stirrers, tubing for corrosive chemicals, and thread seal tape in plumbing applications (plumbers tape). A summary of the physical properties of PTFE is given in Table 7.10. PTFE is synthesized by the emulsion polymerization of tetrafluoroethylene monomer under pressure through free radical catalyst, (7.45).



(7.45)

Property	**Value**
Density	2.2 g/cm^3
Melting point	327 °C
Young's modulus	0.5 GPa
Yield strength	23 MPa
Coefficient of friction	0.05 - 0.10
Dielectric constant	2.1
Dielectric strength (1 MHz)	60 MV/m

Table 7.10: Physical properties of poly(tetrafluoroethylene) (PTFE).

In contrast with PTFE, octafluoroisobutylene, $(CF_3)_2C{=}CF_2$, is highly toxic, while perfluorodecahydronapthalene ($C_{10}F_8$, Figure 7.52) is used as a blood substitute component.

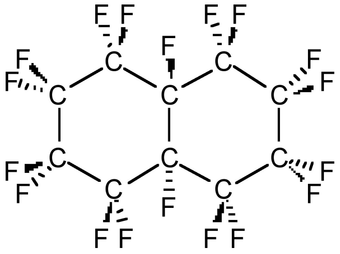


Figure 7.52: Structure of perfluorodecahydronapthalene.

7.2.5.3 Mixed halides

Mixed halides are an important class of halocarbon compound. They are synthesized by halide exchange, (7.46). The high cost of SbF_3 means that the reaction is generally run with an excess of the chloride.

$$3\ CCl_4 + 2\ SbF_3 \rightarrow 2\ CCl_2F_2 + 2\ SbCl_3 \quad (7.46)$$

The ordinary name for mixed carbon halide is halon or Freon, although Freon is actually a Du Pont trademark. A list of selected Freon compounds are given in Table 7.11. Halons are non-toxic, non-flammable, and have no odor. However, it is their very lack of reactivity that has caused a problem.

Freon	**Formula**	**Uses**
12	CCl_2F_2	Refrigerant
11	CCl_3F	Refrigerant
114	$ClF_2C\text{-}CClF_2$	Refrigerant
113	$Cl_3C\text{-}CF_3$	Solvent
13B1	$CBrF_3$	Fire extinguisher
1211	$CBrClF_2$	Fire extinguisher

Table 7.11: Selected Freons and their applications.

7.2.5.3.1 Environmental impact of chlorofluorcarbon compounds (CFCs)

Chlorofluorcarbon compounds (CFCs) are very stable and are not degraded in the environment. As a consequence they are transported to the stratosphere where they decomposed upon photolysis, (7.47). The resulting chloride radical is a catalyst for the decomposition of ozone, (7.48), as well as a catalyst for the reaction of ozone with molecular oxygen, (7.49).

$$CCl_2F_2 + h\nu \rightarrow {\cdot}CClF_2 + Cl{\cdot} \quad (7.47)$$

$$2\ O_3 \xrightarrow{Cl\cdot} 3\ O_2 \quad (7.48)$$

$$\mathrm{O_3 + O \xrightarrow{Cl\cdot} 2\,O_2} \tag{7.49}$$

The widespread use of CFCs as refrigerants and propellants meant that by 1986 there were 2.5 billion pounds of CFC being liberated to the atmosphere. This was equivalent to $^{1}/_{2}$. lb per person on the planet. Since the ozone layer provides the vital protection to life on the Earth's surface from high energy UV radiation the release of CFC (along with other chemicals) caused a dramatic change in the ozone layer, including the increase in the polar hole in the ozone layer. As a result of the EU called for a complete ban of CFCs (which was followed by other countries). In their place new chemicals with similar refrigerant properties were developed. These compounds contained C-H bonds (e.g., $C_2HCl_2F_3$ and $C_2H_3Cl_2F$) that are readily broken in the lower atmosphere, thus limiting the transport to the stratosphere.

7.2.5.4 Carbonyl halides

All the carbonyl halides ($X_2C{=}O$, X = F, Cl, Br, I) are known (Table 7.8). Phosgene ($Cl_2C{=}O$) was first synthesized by John Davy (Figure 7.53) in 1812 by exposing a mixture of carbon monoxide and chlorine to sunlight, (7.50). He named it phosgene from the Greek, *phos* (light) and *gene* (born), in reference to use of light to promote the reaction. The fluoride is also prepared by the reaction of carbon monoxide with the halogen, while the bromide is prepared by the partial hydrolysis of CBr_4 with sulfuric acid.

$$\mathrm{CO + Cl_2 \rightarrow Cl_2C{=}O} \tag{7.50}$$

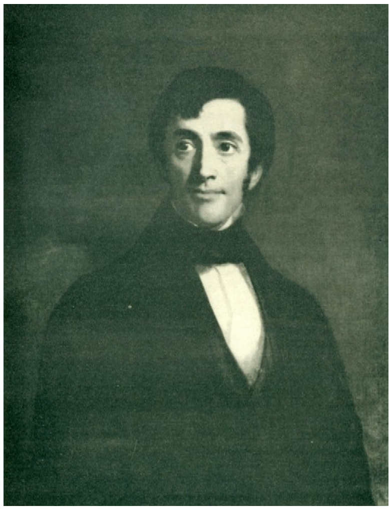


Figure 7.53: British doctor and chemist John Davy FRS (1790 – 1868) was also the brother of the noted chemist Sir Humphry Davy.

The synthesis of isocyanates from alkyl or aryl amines illustrates the electrophilic character of phosgene and its ability to introduce the equivalent of "CO^{2+}", (7.51). This reaction is conducted in the presence of a base such as pyridine that absorbs the hydrogen chloride. Phosgene may also be used to produce acyl chlorides from carboxylic acids, (7.52). However, thionyl chloride is more commonly and more safely used in this reaction.

$$RNH_2 + Cl_2C{=}O \rightarrow RN{=}C{=}O + 2\ HCl \quad (7.51)$$

$$RCO_2H + Cl_2C{=}O \rightarrow RC(O)Cl + HCl + CO_2 \quad (7.52)$$

7.2.5.4.1 Phosgene as a weapon of war

Phosgene is a toxic gas with the smell of “new-mown hay” and was used in chemical warfare during the First World War (Figure 7.54) where it was a more potent weapon than chlorine. While chlorine was potentially deadly it caused the victim to violently cough and choke (the bodies natural defense to limiting inhalation), in contrast, phosgene caused much less coughing with the result that more of it was inhaled. Phosgene often had a delayed effect; apparently healthy soldiers were taken down with phosgene gas poisoning up to 48 hours after inhalation. A fatal dose of phosgene eventually led to shallow breathing and retching, pulse up to 120, an ashen face and the discharge of four pints of yellow liquid from the lungs each hour for the 48 of the drowning spasms.

Figure 7.54: Australian infantry from the 45th Battalion, Australian 4th Division wearing Small Box Respirators (SBR) as protection of chemical warfare agents. Photograph taken at Zonnebeke, on the Ypres sector, 27th September 1917. Copyright: Australian War Memorial.

Although phosgene’s boiling point (7.6 °C) meant that is was a vapor, the so-called "white star" mixture of phosgene and chlorine was commonly used on the Somme, because the chlorine supplied the necessary vapor with which to carry the phosgene. A summary of the casualties inflicted by chemicval warefare agents during the Great War is shown in Table 7.12.

Country	**Total casualties**	**Deaths**
Russia	419,340	56,000
Germany	200,000	9,000
France	190,000	8,000
British Empire	188,706	8,109
Austria-Hungary	100,000	3,000
USA	72,807	1,462
Italy	60,000	4,627
Others	10,000	1,000

Table 7.12: Casualties from gas attacks during the First World War (including chlorine, phosgene, and mustard gas). British Empire includes troops from United Kingdom, Australia, Canada, India, New Zealand, and South Africa.

7.3 Silicon

7.3.1 Comparison Between Silicon and Carbon[10]

An understanding of the differences between carbon and silicon is important in understanding the relative chemistry of these Group 14 elements.

7.3.1.1 Size

As expected silicon is larger than carbon due to the presence of a second shell: i.e., C = $1s^2$ $2s^2$ $2p^2$ while Si = $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^2$. A comparison of the relative sizes of carbon and silicon are given in Table 7.13.

Element	**Atomic radius (Å)**	**Covalent radius sp^3 (Å)**	**van der Waal radius (Å)**
C	0.91	1.11	0.77
Si	1.46	0.76	1.17

Table 7.13: Atomic, covalent, and van der Waals radii of carbon and silicon.

7.3.1.2 Coordination number

Carbon is known to have a coordination number of 2, 3, and 4 in its compounds depending on the hybridization. A coordination number of 1 can also be considered for CO and CN^-. Four-coordinate carbon may be considered to be coordinatively saturated. In contrast, in the absence of overwhelming steric bulk, silicon is observed to have coordination numbers of 3, 4, 5, and 6. Examples of five and six-coordinate silicon include $Si(acac)_2Cl$ and $SiF_6{}^{2-}$, respectively. Coordination numbers of higher than 4 have been ascribed to the use of low-lying *d* orbitals; however, calculations show these are not significant. Instead, hypervalent silicon is better described by the formation of 3-center molecular orbitals, e.g., Figure 7.55.

> NOTE: A hypervalent molecule is a molecule that contains one or more typical elements (Group 1, 2, 13-18) formally bearing more than eight electrons in their valence shells.

---

[10] This content is available online at <http://cnx.org/content/m32945/1.2/>.

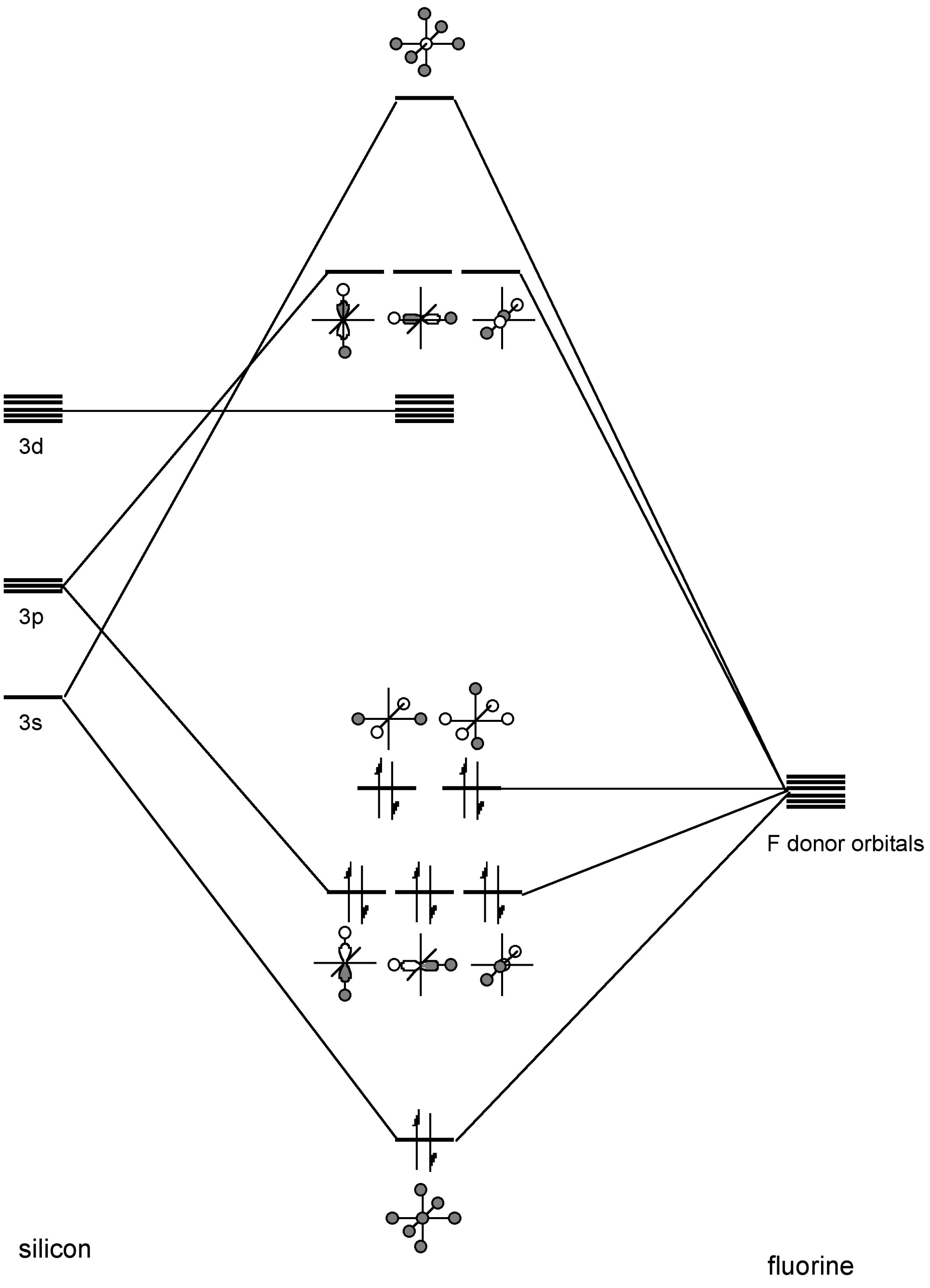


Figure 7.55: Molecular orbital diagram for SiF_6^{2-}.

7.3.1.3 Electronegativity

The electronegativities of silicon and carbon are given in Table along with hydrogen. Since carbon is more electronegative than hydrogen the C-H bond is polarized towards carbon resulting in a more protic hydrogen (Figure 7.56a). In contrast, the lower electronegativity of silicon results in a more hydridic hydrogen (Figure 7.56b). This difference is reflected in the reaction chemistry of SiH_4 versus CH_4.

Element	**Pauling scale**
C	2.5
H	2.1
Si	1.8

Table 7.14: Selected Pauling electronegativity values.

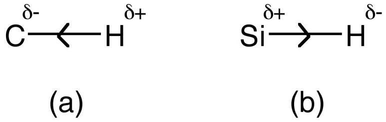


Figure 7.56: Relative polarization of C-H and Si-H bonds.

7.3.1.4 Bond energies

The E-E and E-O bond energies for carbon and silicon are given in Table 7.15. The bond energy for a C-C bond is slightly greater than for a C-O bond, while the Si-O bond is significantly stronger than the Si-Si bond. This difference is reflected in the chemistry of silicon versus carbon compounds. The chemistry of carbon is dominated by catenation: the ability of a chemical element to form a long chain-like structure via a series of covalent bonds. Although silicon does form Si-Si bonds, they are far more reactive than their C-C analogs, and polymers of silicon are predominantly comprised of Si-O chains (as a result of the very strong bond).

Element	**E-E bond energy (kJ/mol)**	**E-O bond energy (kJ/mol)**
C	356	335
Si	230	370

Table 7.15: Selected bond energies for carbon and silicon.

7.3.1.5 Multiple bonds

While unsaturated compounds for carbon (i.e., alkenes and alkynes) are common, the analogous silicon compounds (disilenes) were only reported in 1981, and disilynes in 2004. The Si=Si double bond lengths are 2.14 - 2.29 Å which is 5 - 10% shorter than the Si-Si single bond lengths. This bond shortening is less than *ca.* 13% in carbon compounds.

> NOTE: The traditional lack of multiple bonds for the Period 3 elements and lower led to the formulation of the double bond rule which states that *chemical elements with a principal quantum number greater than 2 do not form multiple bonds (e.g., double bonds and triple bonds) with themselves or with other elements*. This rule was made obsolete starting from 1981 with the discovery of silicon and phosphorus double bonds. Double bonds that would ordinarily not form can be stabilized with proper functional groups through kinetic stabilization, i.e., either electronically or sterically.

7.3.1.6 Bibliography

- R. West, M. J. Fink, and J. Michl, *Science*, 1981, **214**, 1343.
- A. Sekiguchi, R. Kinjo, and M. Ichinohe, *Science*, 2004, **305**, 1755.

7.3.2 Silicon and Silica as Electronic Materials

7.3.2.1 Semiconductor Grade Silicon[11]

7.3.2.1.1 Introduction

The synthesis and purification of bulk polycrystalline semiconductor material represents the first step towards the commercial fabrication of an electronic device. This polycrystalline material is then used as the raw material for the formation of single crystal material that is processed to semiconductor wafers. The strong influence on the electric characteristics of a semiconductors exhibited by small amounts of some impurities requires that the bulk raw material be of very high purity ($> 99.9999\%$). Although some level of purification is possible during the crystallization process it is important to use as high a purity starting material as possible.

Following oxygen (46%), silicon (L. silicis flint) is the most abundant element in the earth's crust (28%). However, silicon does not occur in its elemental form, but as its oxide (SiO_2) or as silicates. Sand, quartz, amethyst, agate, flint, and opal are some of the forms in which the oxide appears. Granite, hornblende, asbestos, feldspar, clay and mica, etc. are a few of the numerous silicate minerals. With such boundless supplies of the raw material, the costs associated with the production of bulk silicon is not one of abstraction and conversion of the oxide(s), but of purification of the crude elemental silicon. While 98% elemental silicon, known as metallurgical-grade silicon (MGS), is readily produced on a large scale, the requirements of extreme purity for electronic device fabrication require additional purification steps in order to produce electronic-grade silicon (EGS). Electronic-grade silicon is also known as semiconductor-grade silicon (SGS). In order for the purity levels to be acceptable for subsequent crystal growth and device fabrication, EGS must have carbon and oxygen impurity levels less than a few parts per million (ppm), and metal impurities at the parts per billion (ppb) range or lower. Table 7.16 and Table 7.17 give typical impurity concentrations in MGS and EGS, respectively. Besides the purity, the production cost and the specifications must meet the industry desires.

---

[11] This content is available online at <http://cnx.org/content/m31994/1.3/>.

Element	**Concentration (ppm)**	**Element**	**Concentration (ppm)**
aluminum	1000-4350	manganese	50-120
boron	40-60	molybdenum	< 20
calcium	245-500	nickel	10-105
chromium	50-200	phosphorus	20-50
copper	15-45	titanium	140-300
iron	1550-6500	vanadium	50-250
magnesium	10-50	zirconium	20

Table 7.16: Typical impurity concentrations found in metallurgical-grade silicon (MGS).

Element	**Concentration (ppb)**	**Element**	**Concentration (ppb)**
arsenic	< 0.001	gold	< 0.00001
antimony	< 0.001	iron	0.1-1.0
boron	≤ 0.1	nickel	0.1-0.5
carbon	100-1000	oxygen	100-400
chromium	< 0.01	phosphorus	≤ 0.3
cobalt	0.001	silver	0.001
copper	0.1	zinc	< 0.1

Table 7.17: Typical impurity concentrations found in electronic-grade silicon (EGS).

7.3.2.1.2 Metallurgical-grade silicon (MGS)

The typical source material for commercial production of elemental silicon is quartzite gravel; a relatively pure form of sand (SiO_2). The first step in the synthesis of silicon is the melting and reduction of the silica in a submerged-electrode arc furnace. An example of which is shown schematically in Figure 7.57, along with the appropriate chemical reactions. A mixture of quartzite gravel and carbon are heated to high temperatures (ca. 1800 °C) in the furnace. The carbon bed consists of a mixture of coal, coke, and wood chips. The latter providing the necessary porosity such that the gases created during the reaction (SiO and CO) are able to flow through the bed.

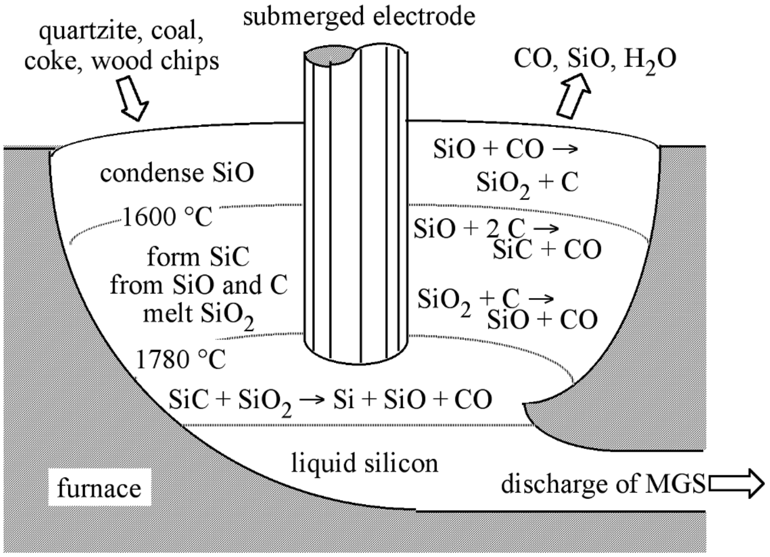


Figure 7.57: Schematic of submerged-electrode arc furnace for the production of metallurgical-grade silicon (MGS).

The overall reduction reaction of SiO_2 is expressed in (7.53), however, the reaction sequence is more complex than this overall reaction implies, and involves the formation of SiC and SiO intermediates. The initial reaction between molten SiO_2 and C, (7.54), takes place in the arc between adjacent electrodes, where the local temperature can exceed 2000 °C. The SiO and CO thus generated flow to cooler zones in the furnace where SiC is formed, (7.55), or higher in the bed where they reform SiO_2 and C, (7.54). The SiC reacts with molten SiO_2, (7.56), producing the desired silicon along with SiO and CO. The molten silicon formed is drawn-off from the furnace and solidified.

$$SiO_2(\text{liquid}) + 2\ C(\text{solid}) \rightarrow Si(\text{liquid}) + 2\ CO\ (\text{gas}) \quad (7.53)$$

$$SiO_2 + 2\ C \underset{<1600\ ^\circ C}{\overset{>1700\ ^\circ C}{\rightleftharpoons}} SiO + CO \quad (7.54)$$

$$SiO + 2\ C \rightarrow SiC + CO\ (1600 - 1700\ ^\circ C) \quad (7.55)$$

$$SiC + SiO_2 \rightarrow Si + SiO + CO \quad (7.56)$$

The as-produced MGS is approximately 98-99% pure, with the major impurities being aluminum and iron (Table 7.16), however, obtaining low levels of boron impurities is of particular importance, because it is difficult to remove and serves as a dopant for silicon. The drawbacks of the above process are that it is energy and raw material intensive. It is estimated that the production of one metric ton (1,000 kg) of MGS requires 2500 - 2700 kg quartzite, 600 kg charcoal, 600 - 700 kg coal or coke, 300 - 500 kg wood chips, and

500,000 kWh of electric power. Currently, approximately 500,000 metric tons of MGS are produced per year, worldwide. Most of the production (ca. 70%) is used for metallurgical applications (e.g., aluminum-silicon alloys are commonly used for automotive engine blocks) from whence its name is derived. Applications in a variety of chemical products such as silicone resins account for about 30%, and only 1% or less of the total production of MGS is used in the manufacturing of high-purity EGS for the electronics industry. The current worldwide consumption of EGS is approximately 5 x 10^6 kg per year.

7.3.2.1.3 Electronic-grade silicon (EGS)

Electronic-grade silicon (EGS) is a polycrystalline material of exceptionally high purity and is the raw material for the growth of single-crystal silicon. EGS is one of the purest materials commonly available, see Table 7.17. The formation of EGS from MGS is accomplished through chemical purification processes. The basic concept of which involves the conversion of MGS to a volatile silicon compound, which is purified by distillation, and subsequently decomposed to re-form elemental silicon of higher purity (i.e., EGS). Irrespective of the purification route employed, the first step is physical pulverization of MGS followed by its conversion to the volatile silicon compounds.

A number of compounds, such as monosilane (SiH_4), dichlorosilane (SiH_2Cl_2), trichlorosilane ($SiHCl_3$), and silicon tetrachloride ($SiCl_4$), have been considered as chemical intermediates. Among these, $SiHCl_3$ has been used predominantly as the intermediate compound for subsequent EGS formation, although SiH_4 is used to a lesser extent. Silicon tetrachloride and its lower chlorinated derivatives are used for the chemical vapor deposition (CVD) growth of Si and SiO_2. The boiling points of silane and its chlorinated products (Table 7.18) are such that they are conveniently separated from each other by fractional distillation.

Compound	**Boiling point (°C)**
SiH_4	-112.3
SiH_3Cl	-30.4
SiH_2Cl_2	8.3
$SiHCl_3$	31.5
$SiCl_4$	57.6

Table 7.18: Boiling points of silane and chlorosilanes at 760 mmHg (1 atmosphere).

The reasons for the predominant use of $SiHCl_3$ in the synthesis of EGS are as follows:

1. $SiHCl_3$ can be easily formed by the reaction of anhydrous hydrogen chloride with MGS at reasonably low temperatures (200 - 400 °C);
2. it is liquid at room temperature so that purification can be accomplished using standard distillation techniques;
3. it is easily handled and if dry can be stored in carbon steel tanks;
4. its liquid is easily vaporized and, when mixed with hydrogen it can be transported in steel lines without corrosion;
5. it can be reduced at atmospheric pressure in the presence of hydrogen;
6. its deposition can take place on heated silicon, thus eliminating contact with any foreign surfaces that may contaminate the resulting silicon; and
7. it reacts at lower temperatures (1000 - 1200 °C) and at faster rates than does $SiCl_4$.

7.3.2.1.3.1 Chlorosilane (Seimens) process

Trichlorosilane is synthesized by heating powdered MGS with anhydrous hydrogen chloride (HCl) at around 300 °C in a fluidized-bed reactor, (7.57).

$$\text{Si(solid)} + 3\ \text{HCl(gas)} \underset{>900\ ^{\circ}\text{C}}{\overset{\text{ca. } 300\ ^{\circ}\text{C}}{\rightleftharpoons}} \text{SiHCl}_3\text{(vapor)} + \text{H}_2\ \text{(gas)} \qquad (7.57)$$

Since the reaction is actually an equilibrium and the formation of $SiHCl_3$ highly exothermic, efficient removal of generated heat is essential to assure a maximum yield of $SiHCl_3$. While the stoichiometric reaction is that shown in (7.57), a mixture of chlorinated silanes is actually prepared which must be separated by fractional distillation, along with the chlorides of any impurities. In particular iron, aluminum, and boron are removed as $FeCl_3$ (b.p. = 316 °C), $AlCl_3$ (m.p. = 190 °C subl.), and BCl_3 (b.p. = 12.65 °C), respectively. Fractional distillation of $SiHCl_3$ from these impurity halides result in greatly increased purity with a concentration of electrically active impurities of less than 1 ppb.

EGS is prepared from purified $SiHCl_3$ in a chemical vapor deposition (CVD) process similar to the epitaxial growth of Si. The high-purity $SiHCl_3$ is vaporized, diluted with high-purity hydrogen, and introduced into the Seimens deposition reactor, shown schematically in Figure 7.58. Within the reactor, thin silicon rods called slim rods (ca. 4 mm diameter) are supported by graphite electrodes. Resistance heating of the slim rods causes the decomposition of the $SiHCl_3$ to yield silicon, as described by the reverse reaction shown in (7.57).

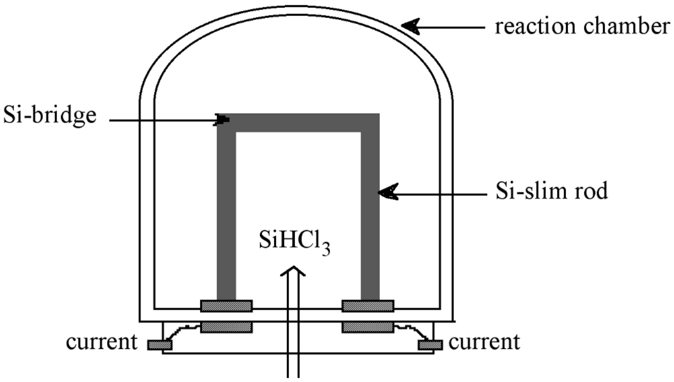


Figure 7.58: Schematic representation of a Seimens deposition reactor.

The shift in the equilibrium from forming $SiHCl_3$ from Si at low temperature, to forming Si from $SiHCl_3$ at high temperature is as a consequence of the temperature dependence, (7.58), of the equilibrium constant, (7.59) where ρ = partial pressure, for (7.57). Since the formation of $SiHCl_3$ is exothermic, i.e., $\Delta H < 0$, an increase in the temperature causes the partial pressure of $SiHCl_3$ to decrease. Thus, the Siemens process is typically run at ca. 1100 °C, while the reverse fluidized bed process is carried out at 300 °C.

$$\ln K_p = \frac{-\Delta H}{RT} \qquad (7.58)$$

$$K_p = \frac{\rho_{SiHCl_3}\ \rho_{H_2}}{\rho_{HCl}} \tag{7.59}$$

The slim rods act as a nucleation point for the deposition of silicon, and the resulting polycrystalline rod consists of columnar grains of silicon (polysilicon) grown perpendicular to the rod axis. Growth occurs at less than 1 mm per hour, and after deposition for 200 to 300 hours high-purity (EGS) polysilicon rods of 150 - 200 mm in diameter are produced. For subsequent float-zone refining the polysilicon EGS rods are cut into long cylindrical rods. Alternatively, the as-formed polysilicon rods are broken into chunks for single crystal growth processes, for example Czochralski melt growth.

In addition to the formation of silicon, the HCl coproduct reacts with the $SiHCl_3$ reactant to form silicon tetrachloride ($SiCl_4$) and hydrogen as major byproducts of the process, (7.60). This reaction represents a major disadvantage with the Seimens process: poor efficiency of silicon and chlorine consumption. Typically, only 30% of the silicon introduced into CVD reactor is converted into high-purity polysilicon.

$$HCl + SiHCl_3 \rightarrow SiCl_4 + H_2 \tag{7.60}$$

In order to improve efficiency the HCl, $SiCl_4$, H_2, and unreacted $SiHCl_3$ are separated and recovered for recycling. Figure 7.59 illustrates the entire chlorosilane process starting with MGS and including the recycling of the reaction byproducts to achieve high overall process efficiency. As a consequence, the production cost of high-purity EGS depends on the commercial usefulness of the byproduct, $SiCl_4$. Additional disadvantages of the Seimens process are derived from its relatively small batch size, slow growth rate, and high power consumption. These issues have lead to the investigation of alternative cost efficient routes to EGS.

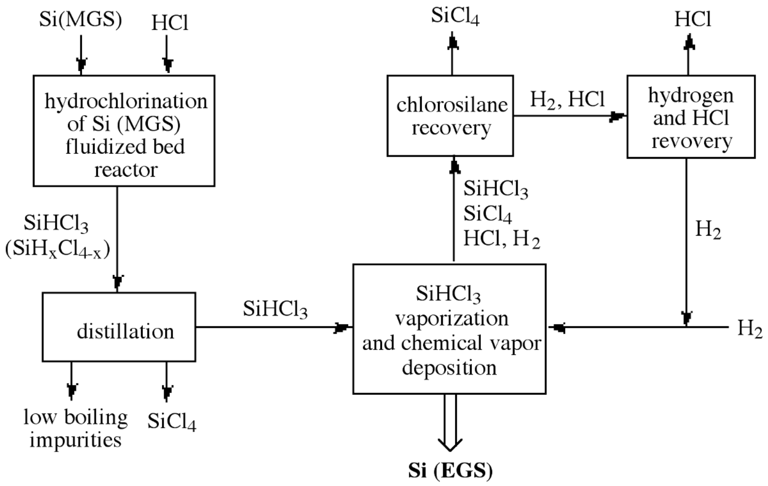


Figure 7.59: Schematic representation of the reaction pathways for the formation of EGS using the chlorosilane process.

7.3.2.1.3.2 Silane process

An alternative process for the production of EGS that has begun to receive commercial attention is the pyrolysis of silane (SiH_4). The advantages of producing EGS from SiH_4 instead of $SiHCl_3$ are potentially lower costs associated with lower reaction temperatures, and less harmful byproducts. Silane decomposes < 900 °C to give silicon and hydrogen, (7.61).

$$SiH_4\text{(vapor)} \rightarrow \text{Si(solid)} + 2\ H_2\text{(gas)} \tag{7.61}$$

Silane may be prepared by a number of routes, each having advantages with respect to purity and production cost. The simplest process involves the direct reaction of MGS powders with magnesium at 500 °C in a hydrogen atmosphere, to form magnesium silicide (Mg_2Si). The magnesium silicide is then reacted with ammonium chloride in liquid ammonia below 0 °C, (7.62).

$$Mg_2Si + 4\ NH_4Cl \rightarrow SiH_4 + 2\ MgCl_2 + 5\ NH_3 \tag{7.62}$$

This process is ideally suited to the removal of boron impurities (a p-type dopant in Si), because the diborane (B_2H_6) produced during the reaction forms the Lewis acid-base complex, $H_3B(NH_3)$, whose volatility is sufficiently lower than SiH_4, allowing for the purification of the latter. It is possible to prepare EGS with a boron content of $\leq$ 20 ppt using SiH_4 synthesized in this manner. However, phosphorus (another dopant) in the form of PH_3 may be present as a contaminant requiring subsequent purification of the SiH_4.

Alternative routes to SiH_4 involve the chemical reduction of $SiCl_4$ by either lithium hydride, (7.63), lithium aluminum hydride, (7.64), or via hydrogenation in the presence of elemental silicon, (7.65) - (7.68). The hydride reduction reactions may be carried-out on relatively large scales (ca. 50 kg), but only batch processes. In contrast, Union Carbide has adapted the hydrogenation to a continuous process, involving disproportionation reactions of chlorosilanes, (7.66) - (7.68), and the fractional distillation of silane, Table 7.18.

$$SiCl_4 + 4\ LiH \rightarrow SiH_4 + 4\ LiCl \tag{7.63}$$

$$SiCl_4 + 4\ LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3 \tag{7.64}$$

$$SiCl_4 + 2\ H_2 + \text{Si(98\%)} \rightarrow 4\ SiHCl_3 \tag{7.65}$$

$$2\ SiHCl_3 \rightarrow SiH_2Cl_2 + SiCl_4 \tag{7.66}$$

$$3\ SiH_2Cl_2 \rightarrow SiH_3Cl + 2\ SiHCl_3 \tag{7.67}$$

$$2\ SiH_3Cl \rightarrow SiH_4 + SiH_2Cl_2 \tag{7.68}$$

Pyrolysis of silane on resistively heated polysilicon filaments at 700 - 800 °C yields polycrystalline EGS. As noted above, the EGS formed has remarkably low boron impurities compared with material prepared from trichlorosilane. Moreover, the resulting EGS is less contaminated with transition metals from the reactor container because SiH_4 decomposition does not cause as much of a corrosion problem as is observed with halide precursor compounds.

7.3.2.1.3.3 Granular polysilicon deposition

Both the chlorosilane (Seimens) and silane processes result in the formation of rods of EGS. However, there has been increased interest in the formation of granular polycrystalline EGS. This process was developed in 1980's, and relies on the decomposition of SiH_4 in a fluidized-bed deposition reactor to produce free-flowing granular polysilicon.

Tiny silicon particles are fluidized in a SiH_4/H_2 flow, and act as seed crystal onto which polysilicon deposits to form free-flowing spherical particles. The size distribution of the particles thus formed is over the range from 0.1 to 1.5 mm in diameter with an average particle size of 0.7 mm. The fluidized-bed seed particles are originally made by grinding EGS in a ball (or hammer) mill and leaching the product with acid, hydrogen peroxide, and water. This process is time-consuming and costly, and tended to introduce undesirable impurities from the metal grinders. In a new method, large EGS particles are fired at each other by a high-speed stream of inert gas and the collision breaks them down into particles of suitable size for a fluidized bed. This process has the main advantage that it introduces no foreign materials and requires no leaching or other post purification.

The fluidized-bed reactors are much more efficient than traditional rod reactors as a consequence of the greater surface area available during CVD growth of silicon. It has been suggested that fluidized-bed reactors require $^1/_5$ to $^1/_{10}$ the energy, and half the capital cost of the traditional process. The quality of fluidized-bed polysilicon has proven to be equivalent to polysilicon produced by the conventional methods. Moreover, granular EGS in a free-flowing form, and with high bulk density, enables crystal growers to obtain the high, reproducible production yields out of each crystal growth run. For example, in the Czochralski crystal growth process, crucibles can be quickly and easily filled to uniform loading with granular EGS, which typically exceed those of randomly stacked polysilicon chunks produced by the Siemens silane process.

7.3.2.1.4 Zone refining

The technique of zone refining is used to purify solid materials and is commonly employed in metallurgical refining. In the case of silicon may be used to obtain the desired ultimate purity of EGS, which has already been purified by chemical processes. Zone refining was invented by Pfann, and makes use of the fact that the equilibrium solubility of any impurity (e.g., Al) is different in the solid and liquid phases of a material (e.g., Si). For the dilute solutions, as is observed in EGS silicon, an equilibrium segregation coefficient (k_0) is defined by $k_0 = C_s/C_l$, where C_s and C_l are the equilibrium concentrations of the impurity in the solid and liquid near the interface, respectively.

If k_0 is less than 1 then the impurities are left in the melt as the molten zone is moved along the material. In a practical sense a molten zone is established in a solid rod. The zone is then moved along the rod from left to right. If $k_0 < 1$ then the frozen part left on the trailing edge of the moving molten zone will be purer than the material that melts in on the right-side leading edge of the moving molten zone. Consequently the solid to the left of the molten zone is purer than the solid on the right. At the completion of the first pass the impurities become concentrated to the right of the solid sample. Repetition of the process allows for purification to exceptionally high levels. Table 7.19. lists the equilibrium segregation coefficients for common impurity and dopant elements in silicon; it should be noted that they are all less than 1.

Element	$\mathbf{k_0}$	**Element**	$\mathbf{k_0}$
aluminum	0.002	iron	8×10^{-6}
boron	0.8	oxygen	0.25
carbon	0.07	phosphorus	0.35
copper	4×10^{-6}	antimony	0.023

Table 7.19: Segregation coefficients for common impurity and dopant elements in silicon.

7.3.2.1.5 Bibliography

- K. G. Baraclough, K. G., in *The Chemistry of the Semiconductor Industry*, Eds. S. J. Moss and A. Ledwith, Blackie and Sons, Glasgow, Scotland (1987).
- L. D. Crossman and J. A. Baker, *Semiconductor Silicon 1977*, Electrochem. Soc., Princeton, New Jersey (1977).
- W. C. O'Mara, Ed. *Handbook of Semiconductor Silicon Technology*, Noyes Pub., New Jersey (1990).
- W. G. Pfann, *Zone Melting*, John Wiley & Sons, New York, (1966).
- F. Shimura, *Semiconductor Silicon Crystal Technology*, Academic Press (1989).

7.3.2.2 Oxidation of Silicon[12]

> NOTE: This module was developed as part of the Rice University course CHEM-496: *Chemistry of Electronic Materials*. This module was prepared with the assistance of Andrea Keys.

7.3.2.2.1 Introduction

In the fabrication of integrated circuits (ICs), the oxidation of silicon is essential, and the production of superior ICs requires an understanding of the oxidation process and the ability to form oxides of high quality. Silicon dioxide has several uses:

1. Serves as a mask against implant or diffusion of dopant into silicon.
2. Provides surface passivation.
3. Isolates one device from another (dielectric isolation).
4. Acts as a component in MOS structures.
5. Provides electrical isolation of multi-level metallization systems.

Methods for forming oxide layers on silicon have been developed, including thermal oxidation, wet anodization, chemical vapor deposition (CVD), and plasma anodization or oxidation. Generally, CVD is used when putting the oxide layer on top of a metal surface, and thermal oxidation is used when a low-charge density level is required for the interface between the oxide and the silicon surface.

7.3.2.2.2 Oxidation of silicon

Silicon's surface has a high affinity for oxygen and thus an oxide layer rapidly forms upon exposure to the atmosphere. The chemical reactions which describe this formation are:

$$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)} \tag{7.69}$$

$$Si_{(s)} + 2\,H_2O_{(g)} \rightarrow SiO_{2(s)} + 2\,H_{2(g)} \tag{7.70}$$

In the first reaction a dry process is utilized involving oxygen gas as the oxygen source and the second reaction describes a wet process which uses steam. The dry process provides a "good" silicon dioxide but is slow and mostly used at the beginning of processing. The wet procedure is problematic in that the purity of the water used cannot be guaranteed to a suitable degree. This problem can be easily solved using a pyrogenic technique which combines hydrogen and oxygen gases to form water vapor of very high purity. Maintaining reagents of high quality is essential to the manufacturing of integrated circuits, and is a concern which plagues each step of this process.

---

[12] This content is available online at <http://cnx.org/content/m24908/1.3/>.

The formation of the oxide layer involves shared valence electrons between silicon and oxygen, which allows the silicon surface to rid itself of "dangling" bonds, such as lone pairs and vacant orbitals, Figure 7.60. These vacancies create mid-gap states between the valence and conduction bands, which prevents the desired band gap of the semiconductor. The Si-O bond strength is covalent (strong), and so can be used to achieve the loss of mid-gap states and passivate the surface of the silicon.

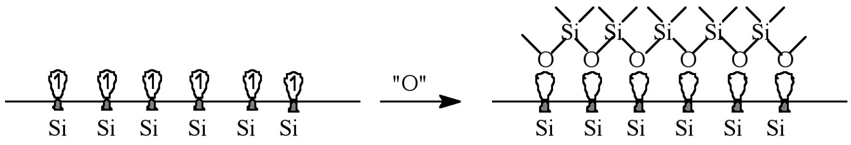


Figure 7.60: Removal of dangling bonds by oxidation of surface.

The oxidation of silicon occurs at the silicon-oxide interface and consists of four steps:

Step 1. Diffusive transport of oxygen across the diffusion layer in the vapor phase adjacent to the silicon oxide-vapor interface.
Step 2. Incorporation of oxygen at the outer surface into the silicon oxide film.
Step 3. Diffusive transport across the silicon oxide film to its interface with the silicon lattice.
Step 4. Reaction of oxygen with silicon at this inner interface.

As the Si-SiO_2 interface moves into the silicon its volume expands, and based upon the densities and molecular weights of Si and SiO_2, 0.44 Å Si is used to obtain 1.0 Å SiO_2.

7.3.2.2.2.1 Pre-oxidation cleaning

The first step in oxidizing a surface of silicon is the removal of the native oxide which forms due to exposure to open air. This may seem redundant to remove an oxide only to put on another, but this is necessary since uncertainty exists as to the purity of the oxide which is present. The contamination of the native oxide by both organic and inorganic materials (arising from previous processing steps and handling) must be removed to prevent the degradation of the essential electrical characteristics of the device. A common procedure uses a H_2O-H_2O_2-NH_4OH mixture which removes the organics present, as well as some group I and II metals. Removal of heavy metals can be achieved using a H_2O-H_2O_2-HCl mixture, which complexes with the ions which are formed. After removal of the native oxide, the desired oxide can be grown. This growth is useful because it provides: chemical protection, conditions suitable for lithography, and passivation. The protection prevents unwanted reactions from occurring and the passivation fills vacancies of bonds on the surface not present within the interior of the crystal. Thus the oxidation of the surface of silicon fulfills several functions in one step.

7.3.2.2.2.2 Thermal oxidation

The growth of oxides on a silicon surface can be a particularly tedious process, since the growth must be uniform and pure. The thickness wanted usually falls in the range 50 - 500 Å, which can take a long time and must be done on a large scale. This is done by stacking the silicon wafers in a horizontal quartz tube while the oxygen source flows over the wafers, which are situated vertically in a slotted paddle (boat), see Figure 7.61. This procedure is performed at 1 atm pressure, and the temperature ranges from 700 to 1200 °C, being held to within ±1 °C to ensure uniformity. The choice of oxidation technique depends on the thickness and oxide properties required. Oxides that are relatively thin and those that require low charge at the interface are typically grown in dry oxygen. When thick oxides are required (> 0.5 mm) are desired, steam is the source of choice. Steam can be used at wide range of pressures (1 atm to 25 atm), and the higher pressures allow thick oxide growth to be achieved at moderate temperatures in reasonable amounts of time.

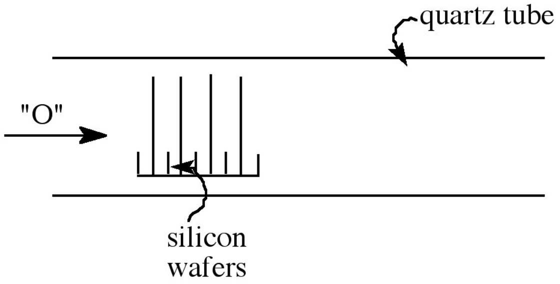


Figure 7.61: Horizontal diffusion tube showing the oxidation of silicon wafers at 1 atm pressure.

The thickness of SiO_2 layers on a Si substrate is readily determined by the color of the film. Table 7.20 provides a guidline for thermal grown oxides.

Film thickness (μm)	**Color**	**Film thickness (μm)**	**Color**
0.05	tan	0.63	violet-red
0.07	brown	0.68	"bluish"
0.10	dark violet to red-violet	0.72	blue-green to gree
0.12	royal blue	0.77	"yellowish"
0.15	light blue to metallic blue	0.80	orange
0.17	metallic to light yellow-green	0.82	salmon
0.20	light gold	0.85	light red-violet
0.22	gold	0.86	violet
0.25	orange to melon	0.87	blue violet

continued on next page

0.27	red-violet	0.89	blue
0.30	blue to violet blue	0.92	blue-green
0.31	blue	0.95	yellow-green
0.32	blue to blue-green	0.97	yellow
0.34	light green	0.99	orange
0.35	green to yellow-green	1.00	carnation pink
0.36	yellow-green	1.02	violet red
0.37	green-yellow	1.05	red-violet
0.39	yellow	1.06	violet
0.41	light orange	1.07	blue-violet
0.42	carnation pink	1.10	green
0.44	violet-red	1.11	yellow-green
0.46	red-violet	1.12	green
0.47	violet	1.18	violet
0.48	blue-violet	1.19	red-violet
0.49	blue	1.21	violet-red
0.50	blue green	1.24	carnation pink to salmon
0.52	green	1.25	orange
0.54	yellow-green	1.28	"yellowish"
0.56	green-yellow	1.32	sky blue to green-blue
0.57	"yellowish"	1.40	orange
0.58	light orange to pink	1.46	blue-violet
0.60	carnation pink	1.50	blue

Table 7.20: Color chart for thermally grown SiO_2 films observed under daylight fluorescent lighting.

7.3.2.2.2.3 High pressure oxidation

High pressure oxidation is another method of oxidizing the silicon surface which controls the rate of oxidation. This is possible because the rate is proportional to the concentration of the oxide, which in turn is proportional to the partial pressure of the oxidizing species, according to Henry's law, (7.71), where C is the equilibrium concentration of the oxide, H is Henry's law constant, and p_O is the partial pressure of the oxidizing species.

$$C = H_{(pO)} \qquad (7.71)$$

This approach is fast, with a rate of oxidation ranging from 100 to 1000 mm/h, and also occurs at a relatively low temperature. It is a useful process, preventing dopants from being displaced and also forms a low number of defects, which is most useful at the end of processing.

7.3.2.2.2.4 Plasma oxidation

Plasma oxidation and anodization of silicon is readily accomplished by the use of activated oxygen as the oxidizing species. The highly reactive oxygen is formed within an electrical discharge or plasma. The oxidation is carried out in a low pressure (0.05 - 0.5 Torr) chamber, and the the plasma is produced either by a DC electron source or a high-frequency discharge. In simple plasma oxidation the sample (i.e., the silicon wafer) is held at ground potential. In contrast, aniodization systems usually have a DC bias between the sample and an electrode with the sample biased positively with respect to the cathode. Platinum electrodes are commonly used as the cathodes.

There have been at least 34 different reactions reported to occur in an oxygen plasma, however, the vast majority of these are inconsequential with respect to the formation of active species. Furthermore, many of the potentially active species are sufficiently short lived that it is unlikely that they make a significant contribution. The primary active species within the oxygen plasma are undoubtedly O^- and O^{2+}. Both being produced in near equal quantities, although only the former is relevant to plasma aniodization. While these species may be active with respect to surface oxidation, it is more likely that an electron transfer occurs from the semiconductor surface yields activated oxygen species, which are the actual reactants in the oxidation of the silicon.

The significant advatage of plasma processes is that while the electron temperature of the ionized oxygen gas is in excess of 10,000 K, the thermal temperatures required are significantly lower than required for the high pressure method, i.e., < 600 °C. The advantages of the lower reaction temperatures include: the minimization of dopant diffusion and the impediment of the generation of defects. Despite these advantages there are two primary disadvantages of any plasma based process. First, the high electric fields present during the processes cause damage to the resultant oxide, in particular, a high density of interface traps often result. However, post annealing may improve film quality. Second, the growth rates of plasma oxidation are low, typically 1000 Å/h. This growth rate is increased by about a factor of 10 for plasma aniodization, and further improvements are observed if 1 - 3% chlorine is added to the oxygen source.

7.3.2.2.2.5 Masking

A selective mask against the diffusion of dopant atoms at high temperatures can be found in a silicon dioxide layer, which can prove to be very useful in integrated circuit processing. A predeposition of dopant by ion implantation, chemical diffusion, or spin-on techniques typically results in a dopant source at or near the surface of the oxide. During the initial high-temperature step, diffusion in the oxide must be slow enough with respect to diffusion in the silicon that the dopants do not diffuse through the oxide in the masked region and reach the silicon surface. The required thickness may be determined by experimentally measuring, at a particular temperature and time, the oxide thickness necessary to prevent the inversion of a lightly doped silicon substrate of opposite conductivity. To this is then added a safety factor, with typical total values ranging from 0.5 to 0.7 mm. The impurity masking properties result when the oxide is partially converted into a silica impurity oxide "glass" phase, and prevents the impurities from reaching the SiO_2-Si interface.

7.3.2.2.3 Bibliography

- M. M. Atalla, in *Properties of Elemental and Compound Semiconductors*, Ed. H. Gatos, Interscience: New York (1960).
- S. K. Ghandhi, *VLSI Fabrication Principles, Silicon and Gallium Arsenide*, Wiley, Chichester, 2nd Ed. (1994).
- S. M. Sze, *Physics of Semiconductor Devices*, 2nd Edition, John Wiley & Sons, New York (1981).
- D. L. Lile, *Solid State Electron.*, 1978, **21**, 1199.
- W. E. Spicer, P. W. Chye, P. R. Skeath, and C. Y. Su, I. Lindau, *J. Vac. Sci. Technol.*, 1979, **16**, 1422.
- V. Q. Ho and T. Sugano, *IEEE Trans. Electron Devices*, 1980, **ED-27**, 1436.
- J. R. Hollanhan and A. T. Bells, *Techniques and Applications of Plasma Chemistry*, Wiley, New York (1974).
- R. P. H. Chang and A. K. Sinha, *Appl. Phys. Lett.*, 1976, **29**, 56.

7.3.2.3 Applications for Silica Thin Films[13]

7.3.2.3.1 Introduction

While the physical properties of silica make it suitable for use in protective and optical coating applications, the biggest application of insulating SiO_2 thin films is undoubtedly in semiconductor devices, in which the insulator performs a number of specific tasks, including: surface passivation, field effect transistor (FET) gate layer, isolation layers, planarization and packaging.

The term insulator generally refers to a material that exhibits low thermal or electrical conductivity; electrically insulating materials are also called dielectrics. It is in regard to the high resistance to the flow of an electric current that SiO_2 thin films are of the greatest commercial importance. The dielectric constant (ε) is a measure of a dielectric materials ability to store charge, and is characterized by the electrostatic energy stored per unit volume across a unit potential gradient. The magnitude of ε is an indication of the degree of polarization or charge displacement within a material. The dielectric constant for air is 1, and for ionic solids is generally in the range of 5 - 10. Dielectric constants are defined as the ratio of the material's capacitance to that of air, i.e., (7.72). The dielectric constant for silicon dioxide ranges from 3.9 to 4.9, for thermally and plasma CVD grown films, respectively.

$$\varepsilon = C_{\text{material}}/C_{\text{air}} \tag{7.72}$$

An insulating layer is a film or deposited layer of dielectric material separating or covering conductive layers. Ideally, in these application an insulating material should have a surface resistivity of greater than 10^{13} Ω/cm^2 or a volume resistivity of greater than 10^{11} Ω.cm. However, for some applications, lower values are acceptable; an electrical insulator is generally accepted to have a resistivity greater than 10^5 Ω.cm. CVD SiO_2 thin films have a resistivity of 10^6 - 10^{16} Ω.cm, depending on the film growth method.

As a consequence of its dielectric properties SiO_2, and related silicas, are used for isolating conducting layers, to facilitate the diffusion of dopants from doped oxides, as diffusion and ion implantation masks, capping doped films to prevent loss of dopant, for gettering impurities, for protection against moisture and oxidation, and for electronic passivation. Of the many methods used for the deposition of thin films, chemical vapor deposition (CVD) is most often used for semiconductor processing. In order to appreciate the unique problems associated with the CVD of insulating SiO_2 thin films it is worth first reviewing some of their applications. Summarized below are three areas of greatest importance to the fabrication of contemporary semiconductor devices: isolation and gate insulation, passivation, and planarization.

7.3.2.3.2 Device isolation and gate insulation

A microcircuit may be described as a collection of devices each consisting of "an assembly of active and passive components, interconnected within a monolithic block of semiconducting material". Each device is required to be isolated from adjacent devices in order to allow for maximum efficiency of the overall circuit. Furthermore within a device, contacts must also be electrically isolated. While there are a number of methods for isolating individual devices within a circuit (reverse-biased junctions, mesa isolation, use of semi-insulating substrates, and oxide isolation), the isolation of the active components in a single device is almost exclusively accomplished by the deposition of an insulator.

In Figure 7.62 is shown a schematic representation of a silicon MOSFET (metal-oxide-semiconductor field effect transistor). The MOSFET is the basic component of silicon-CMOS (complimentary metal-oxide-semiconductor) circuits which, in turn, form the basis for logic circuits, such as those used in the CPU (central processing unit) of a modern personal computer. It can be seen that the MOSFET is isolated from adjacent devices by a reverse-biased junction (p^+-channel stop) and a thick oxide layer. The gate, source and drain contact are electrically isolated from each other by a thin insulating oxide. A similar scheme is used for the isolation of the collector from both the base and the emitter in bipolar transistor devices.

---

[13] This content is available online at <http://cnx.org/content/m24883/1.5/>.

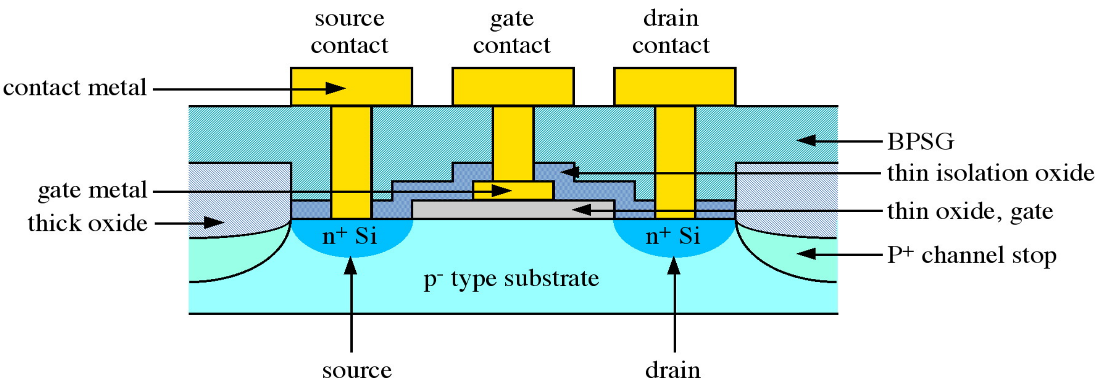


Figure 7.62: Schematic diagrams of a Si-MOSFET (metal-oxide-semiconductor field effect transistor).

As a transistor, a MOSFET has many advantages over alternate designs. The key advantage is low power dissipation resulting from the high impedance of the device. This is a result of the thin insulation layer between the channel (region between source and drain) and the gate contact, see Figure 7.62. The presence of an insulating gate is characteristic of a general class of devices called MISFETs (metal-insulator-semiconductor field effect transistor). MOSFETs are a subset of MISFETs where the insulator is specifically an oxide, e.g., in the case of a silicon MISFET device the insulator is SiO_2, hence MOSFET. It is the fabrication of MOSFET circuits that has allowed silicon technology to dominate digital electronics (logic circuits). However, increases in computing power and speed require a constant reduction in device size and increased complexity in device architecture.

7.3.2.3.3 Passivation

Passivation is often defined as a process whereby a film is grown on the surface of a semiconductor to either (a) chemically protect it from the environment, or (b) provide electronic stabilization of the surface.

From the earliest days of solid state electronics it has been recognized that the presence or absence of surface states plays a decisive role in the usefulness of any semiconducting material. On the surface of any solid state material there are sites in which the coordination environment of the atoms is incomplete. These sites, commonly termed "dangling bonds", are the cause of the electronically active states which allow for the recombination of holes and electrons. This recombination occurs at energies below the bulk value, and interferes with the inherent properties of the semiconductor. In order to optimize the properties of a semiconductor device it is desirable to covalently satisfy all these surface bonds, thereby shifting the surface states out of the band gap and into the valence or conduction bands. Electronic passivation may therefore be described as a process which reduces the density of available electronic states present at the surface of a semiconductor, thereby limiting hole and electron recombination possibilities. In the case of silicon both the native oxide and other oxides admirably fulfill these requirements.

Chemical passivation requires a material that inhibits the diffusion of oxygen, water, or other species to the surface of the underlying semiconductor. In addition, the material is ideally hard and resistant to chemical attack. A perfect passivation material would satisfy both electronic and chemical passivation requirements.

7.3.2.3.4 Planarization

For the vast majority of electronic devices, the starting point is a substrate consisting of a flat single crystal wafer of semiconducting material. During processing, which includes the growth of both insulating and conducting films, the surface becomes increasingly non-planar. For example, a gate oxide in a typical MOSFET (see Figure 7.62) may be typically 100 - 250 Å thick, while the isolation or field oxide may be 10,000 Å. In order for the successful subsequent deposition of conducting layers (metallization) to occur without breaking metal lines (often due to the difficulty in maintaining step coverage), the surface must be flat and smooth. This process is called planarization, and can be carried out by a technique known as sacrificial etchback. The steps for this process are outlined in Figure 7.63. An abrupt step (Figure 7.63a) is coated with a conformal layer of a low melting dielectric, e.g., borophosphorosilicate glass, BPSG (Figure 7.63b), and subsequently a sacrificial organic resin (Figure 7.63c). The sample is then plasma etched such that the resin and dielectric are removed at the same rate. Since the plasma etch follows the contour of the organic resin, a smooth surface is left behind (Figure 7.63d). The planarization process thus reduces step height differentials significantly. In addition regions or valleys between individual metallization elements (vias) can be completely filled allowing for a route to producing uniformly flat surfaces, e.g., the BPSG film shown in Figure 7.62.

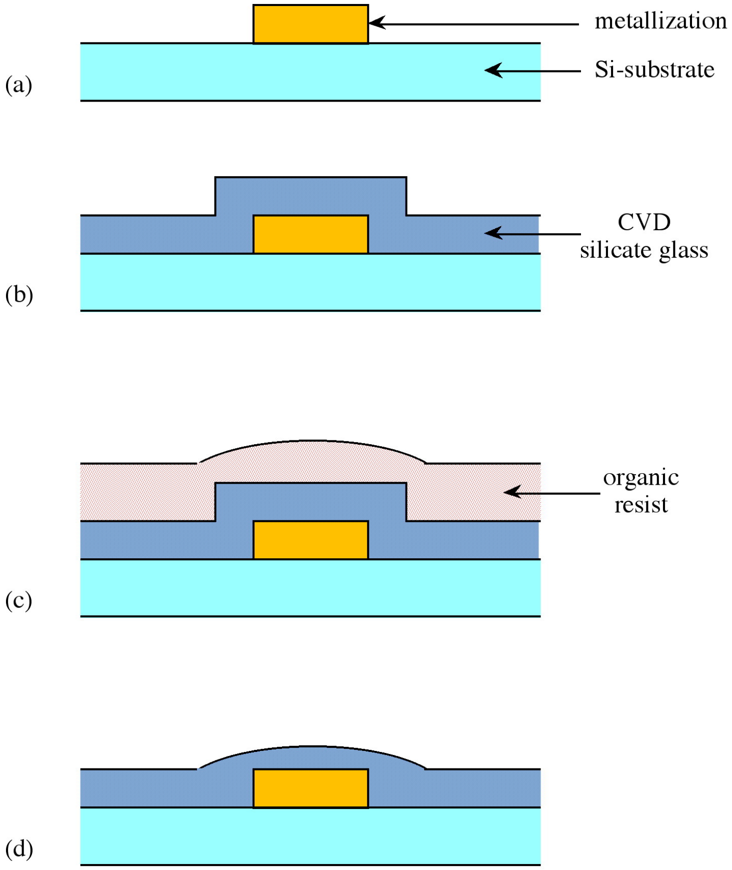


Figure 7.63: Schematic representation of the planarization process. A metallization feature (a) is CVD covered with silicate glass (b), and subsequently coated with an organic resin (c). After etching the resist a smooth silicate surface is produced (d).

The processes of planarization is vital for the development of multilevel structures in VLSI circuits. To minimize interconnection resistance and conserve chip area, multilevel metallization schemes are being developed in which the interconnects run in 3-dimensions.

7.3.2.3.5 Bibliography

- J. L. Vossen and W. Kern, *Phys. Today*, 1980, **33**, 26.
- S. K. Ghandhi, *VLSI Fabrication Principles, Silicon and Gallium Arsenide*, Wiley, Chichester, 2nd Ed. (1994).
- S. M. Sze, *Physics of Semiconductor Devices*, 2nd Edition, John Wiley & Sons, New York (1981).
- W. E. Beadle, J. C. C. Tsai, R. D. Plummer, *Quick Reference Manual for Silicon Integrated Cuircuit Technology*, Wiley, Chichester (1985).
- A. C. Adams and C. D. Capio, *J. Electrochem. Soc.*, 1981, **128**, 2630.