

SILICON AND ITS GLASSY DANCE WITH FLUORINE

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This article delves into the versatile properties of silicon, with a primary focus on its renowned application in glass. Additionally, we examine silicon's susceptibility to fluorine, highlighting fluorine as a global reagent against silicon

1. INTRODUCTION

Silicon is an element located in the third period and group 14 in the periodic table.¹ Its electronic structure is $1s^2 2s^2 2p^6 3s^2 3p^2$. Silicon was used in oxide form in the first human tools.² Attempts to reduce silicon by electrolysis failed. It wasn't until 1822 that Jöns Berzelius obtained a pure form of silicon by heating potassium fluorosilicate with potassium. However, the reaction product was contaminated with potassium silicide, which was removed by stirring with water to obtain silicon powder.

Today, silicon has many applications thanks to its multiple properties and can be found in a variety of forms for a wide range of uses.

This article focuses on two silicon forms : silica, which occurs naturally on Earth and is found in glass, and metallic silicon, which does not occur naturally and must be obtained by reducing silica. Despite all these properties and advantages, silicon, particularly in the form of glass, has a weakness in relation to fluorine, which will be discussed in the last section.

2. SILICA

2.1. Resources

Silicon dioxide presents itself in two primary classifications : crystalline and non-crystalline (amorphous).³ In its crystalline form, this compound occurs naturally as quartz, tridymite, cristobalite, stishovite, and coesite. In contrast, amorphous silica manifests in nature as opal, infusorial earth, and diatomaceous earth. Quartz glass stands as an intermediary state between these structural variations.

2.2. Structures

The most common crystallographic structure of silicates is that of alpha quartz. The crystal system is trigonal and the lattice system is hexagonal. Each silicon (Si^{4+}) is sur-

rounded by 4 oxygen (O^{2-}) in the crystal, forming a chain of tetrahedra linked at the apex.

But there are other, more exotic crystallographic structures, such as beta quartz, which is an allotropic form of silicate. This form of quartz is found mainly in magma where the environment is very hot. It forms at temperatures above 573°C , but on cooling, it reverts to its more common form (alpha quartz).²

Angles (Degree)	$\alpha = 90$	$\beta = 90$	$\gamma = 120$
Lattice parameters ($\text{\AA}$)	$a = 4.92$	$b = 4.92$	$c = 5.43$

Tab. 1 Crystal properties of α -quartz, where a, b, c and α, β, γ are defined in figure 1.

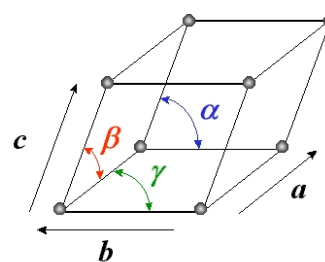


Fig. 1 Crystal lattice ($a, b, c, \alpha, \beta, \gamma$).⁴

2.3. Piezoelectric properties of quartz

Piezoelectricity was discovered in 1880 by the Curie brothers. When a quartz crystal is subjected to stress (an electric force or field), it becomes piezoelectric : it polarises or deforms. These piezoelectric properties are used mainly in watchmaking to produce precision wristwatches.

Quartz crystals belong to the three-two point symmetry group of the trigonal crystal system. Thanks to these crystalline properties, the piezoelectric properties of quartz have been measured. In the quartz crystal, each silicon is

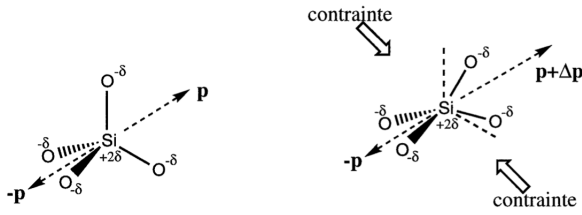


Fig. 2 Silica electronic structure. When the crystal is at rest, the difference in charge between the silicon and oxygen atoms generates an elementary dipole moment for this bond. For an SiO_2 structure, the dipole moment, which is the vector resultant of the elementary moments, is denoted by $\mathbf{p}$. For a tetrahedral structure, the overall dipole moment is zero. When stress (“contrainte” on the schematic) is applied in the direction perpendicular to the plane formed by one of the SiO_2 assemblies, this dipole moment is no longer zero overall; a differential $\Delta\mathbf{p}$ appears. Adapted from [5].

surrounded by four oxygens, forming a tetrahedral structure as explained above. At rest, the overall dipole moment of the tetrahedron is zero, but when stress is applied to the crystal, the tetrahedron deforms, resulting in a non-zero dipole moment and hence polarisation of the crystal, known as crystalline anisotropy.⁵

In figure 2, taken from the literature,⁵ the elementary dipole moments are noted p , and the partial charge is denoted δ . This figure perfectly illustrates the polarisation of the quartz crystal on an atomic scale.

2.4. Glass

2.4.1. Generalities of glass

Glass based on silica is one of the known traditional ceramics, which are a type of ionic solid. In general, this type of ceramic is known for being hard and fragile, with low toughness and ductility but very high compression resistance. They also exhibit high thermal and chemical stability.⁶

In ionic solids, the packing of ions is determined by their relative size (considering the ions as compact spheres of defined radius) and the need to balance electrostatic charges to maintain electrical neutrality. In this case, the main focus is on SiO_2 -based structures, which are known as silicates.⁶

Silicates are among the most abundant element combinations in nature; they are present in soils, rocks, clays, and sands, constituting the majority of them. As mentioned earlier, the unit cell is a tetrahedron with a silicon at the center bonded to four oxygens, forming SiO_4^{4-} . These small SiO_4^{4-} subunits are not ionic since the Si-O bond is covalent. The structures of silicates arise according to different ways of combining in 1, 2, or 3 dimensions.⁶

Silica, the simplest silicate represented as SiO_2 , shows a three-dimensional lattice where all the oxygens of each tetrahedron are shared with adjacent tetrahedra, generating a crystalline structure, as seen in figure 3.⁶

However, in everyday life, the glasses we use are not formed solely by silica but by a modified version. In these cases, the material is no longer an organised crystal but an amorphous solid that includes oxides such as Na_2O , CaO ,

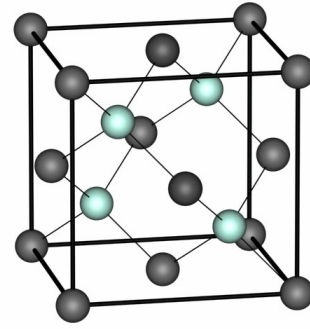


Fig. 3 Silica crystallographic structure. It has the diamond structure, which is two fcc structures shifted along the diagonal with respect to each other. Adapted from [7].

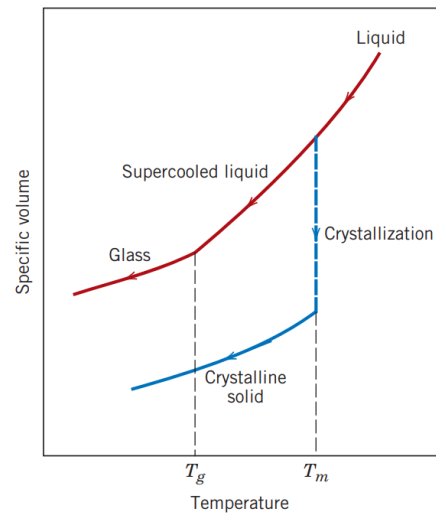


Fig. 4 Contrast of specific volume versus-temperature behavior of crystalline and noncrystalline materials.⁶

Al_2O_3 , MgO , and others, called modifiers.⁶

The addition of oxides modifies the O :Si ratio. If the O :Si ratio increases significantly, the modifiers break the silica lattice. For instance, when Na_2O is added, Na^+ ions enter the lattice voids in the network, preventing vitrification. The added oxygen becomes part of the network, but there is not enough silicon to maintain the lattice intact. Adding modifiers also reduces the melting temperature and viscosity of the glass, enabling its manufacture at lower temperatures.⁶

It is important to note that most silica-based glasses are amorphous solids, not crystalline, as reflected in properties such as the specific volume vs. temperature diagram. Glass does not solidify like crystalline materials. Glasses become increasingly viscous as the temperature decreases. The temperature at which there is a small change in slope is called T_g , or the glass transition temperature. Crystalline materials, by contrast, exhibit an abrupt change at T_M , the melting temperature. For $T < T_g$, the material is a glass. For $T > T_g$, it is a supercooled liquid, and at even higher temperatures, it becomes a liquid.⁶

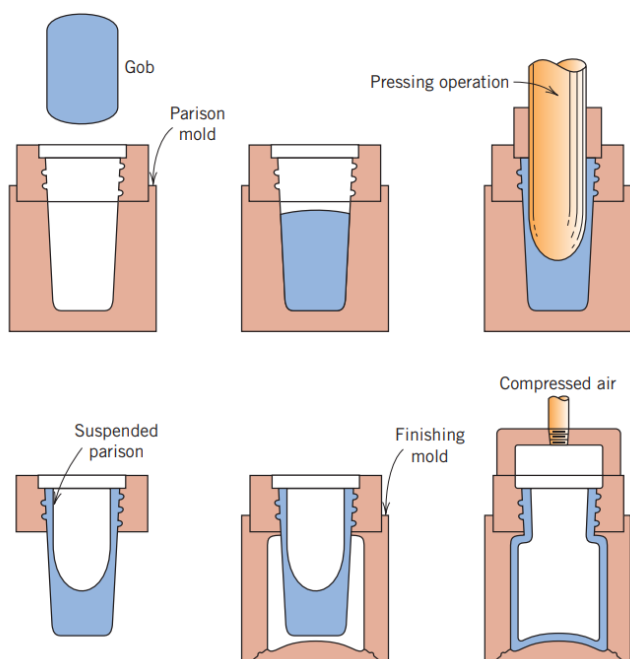


Fig. 5 Glass manufacturing processes.⁶

2.4.2. Glass production

Glass production involves heating raw materials to a temperature that exceeds their melting point. Commercial glasses, mostly silica-soda-lime compositions, commonly utilize quartz sand for silica, while soda ash (Na_2CO_3) and limestone (CaCO_3) provide Na_2O and CaO , respectively. To ensure product quality, especially optical transparency, homogeneity and pore elimination are crucial. Homogeneity is attained through complete melting and mixing, while proper viscosity adjustment absorbs or removes gas bubbles responsible for porosity.⁶

There are four main methods for manufacturing glass products : pressing, blowing, drawing, and fiber forming (Fig. 5). Pressing shapes thick-walled pieces like plates using pressure in a graphite-coated mold. Automation dominates glass blowing for items like jars and bottles ; a gob is mechanically shaped into a parison, then air pressure conforms it to a mold. Drawing forms constant cross-section pieces like sheet, rod, and fibers, achieved by drawing molten glass through orifices. Precise control of glass viscosity, achieved via chamber and orifice temperatures, facilitates the creation of continuous glass fibers in a sophisticated drawing process within a platinum heating chamber.⁶

3. METALLIC SILICON

Metallic silicon is the name we give to large crystals of silicon bonded by covalent bonding. Metallic silicon can be found in different allotropic forms, such as diamond-like structure in atmospheric conditions and beta-stannum-like structure in high-pressure conditions. This change in dimensionality means an increase in coordination index from 4 to 6 and an increase in the metallic character of the element.⁸

3.1. Production

3.1.1. Reduction of Quartz

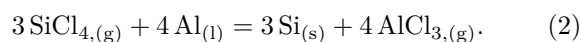
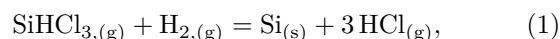
Metallic silicon is largely obtained by reducing silicates. This metallurgical method involves several stages. The aim is to react quartz with carbon in the form of coal or coke.⁸

Firstly, the silicates are reduced in a submerged electric arc furnace, which heats the quartz and the coke to high temperatures. An electric current is passed through the arcs, heating them and allowing the materials to be melted. The process triggers a reaction in which silicon is formed with other gases such as SiO , CO , and CO_2 . The calcium and aluminium impurities contained in the original quartz are removed by treating the melted metal with air. The resulting material is poured into large cast-iron trays and cooled. The result is silicon metal.

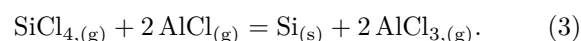
3.1.2. Reduction of Trichlorosilane

Nowadays there are not many natural sources for finding metallic silicon, only in some concrete places such as Taiwan. Therefore, for production in large quantities, we need some complex chemical methods such as the ones based on reduction.⁹

Nowadays, the conventional methods are based on thermal decomposition of minerals and/or H_2 reduction of trichlorosilane (SiHCl_3) (Eq. 1) or thermal decomposition of monosilane (SiH_4) (Eq. 2) :



Nevertheless, equation 2-based processes are, in general, more energetically favorable since the standard Gibbs energy of the reaction is significantly smaller. Recently, there are new methods emerging, such as the ones based on metallothermic reductions involving SiCl_4 , which follow this reaction :



The advantage of these methods is that the by-products they generate (chloride salts) can be recycled by electrochemical decomposition into the reductant metal and Cl_2 gas. In all of these methods, the reaction undergoes purification and refining, formation of the metallic silicon ingots or blocks, and finally, quality control and testing for its final packaging and distribution. Note that purification can be done by chemical processing, zone refining with a silicon rod, or vacuum melting.

3.2. Semiconductive Properties

Metallic silicon is the name we give to large crystals of silicon bonded by covalent bonding. Metallic silicon can be found in different allotropic forms, such as diamond-like structure in atmospheric conditions and β -stannum-like structure in high-pressure conditions. In figure 6, we can see the basic energy band diagram for silicon and carbon in their diamond form. We can observe that silicon's valence band is completely full, and its conduction band is completely empty. We can also observe the bands become

flatter and narrower in silicon, and that they are placed higher on the energetic scale, generating a smaller gap than in carbon and therefore giving the silicon semiconductive properties. This disposition is due to the fact that silicon offers better orbital overlapping, since its orbitals are more diffuse than those in carbon.

The observations mentioned before can be seen experimentally in state density diagrams in figure 7.

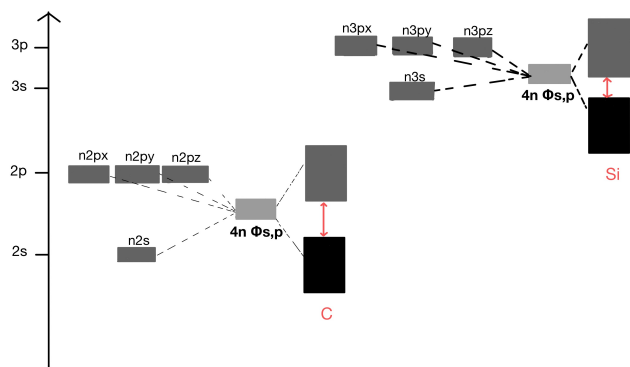


Fig. 6 Band diagram for carbon and silicon. Adapted from [10].

In the diagram, we can see two differentiated zones (bands) with different energy. One corresponds to the bonding orbitals (valence bands) and the other one to the antibonding orbitals (conduction band). As we can see in silicon, both bands are close in energy, which allows electronic transit and therefore semiconductive properties and metallic allure in silicon. This is not the case in the diamond glass-like structure seen in carbon.

These metallic properties can be observed in parameters such as resistivity. The smaller gap in silicon allows current to flow through the material, and therefore we will find less resistivity. We can compare it with similar structures of other elements in the same periodic group, as observed in table 2.

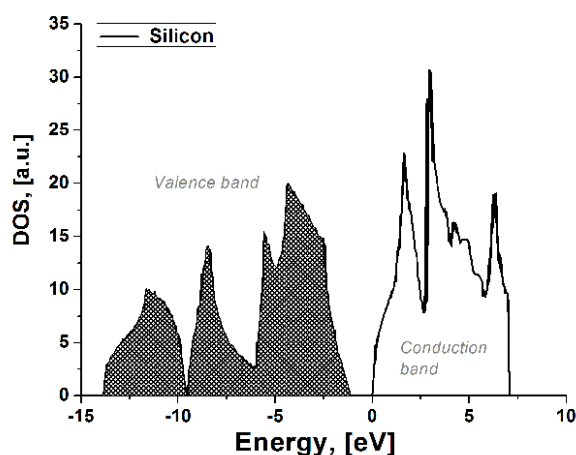


Fig. 7 State density for silicon at different energies.¹¹

Element	Gap (eV)	Resistivity ($\Omega\cdot\text{cm}$)
C (diamond)	6.00	1.0×10^{12}
Si	1.10	2.0
Ge	0.74	0.46

Tab. 2 Band gaps and resistivities of different group IV elements (at 300 K).

4. FLUORINE

It is known as a fact that fluorine dissolves glass (SiO_2), and it is therefore interesting to study the fluorine properties deeper.¹ Fluorine is an element located in the first period and group 17 in the periodic table. Its electronic structure is $1s^2 2s^2 2p^5$. In this group, we can find very little structural diversity. All elements are stable in the form of diatomic molecules. The elements in this group are generally very small and electronically dense, and therefore have a very small coordination index.

Fluorine was initially unidentified by early chemists, who knew that fluorinated metals were composed of an element close to chlorine. The Frenchman André Ampère named this element fluorine. It is found not only in metal complexes but also in fluoride acid. There have been many attempts to isolate fluorine, one of which was the isolation of fluorine from hydrofluoric acid, which sickened the chemist Humphry Davy. In 1869, French chemist Henri Moissan obtained fluorine by electrolysis of potassium bifluoride (KHF_2) dissolved in liquid HF.

In this section, there will be comments about the reactivity of fluorine in general and with structures such as glass, as well as a comparison with other halogens.

4.1. Comparison with other halogens

By the aggregation state, we can see through group 17 that we could have some kind of metallic character. Fluorine and chlorine are gaseous in ordinary conditions, bromine is a liquid, and iodine is a molecular solid.

The orbitals of the elements in this group have very low energies, and therefore the orbital overlapping is very effective, generating mostly diatomic molecules. However, in some cases like iodine, they can form supramolecular structures, in this case layers, which can be stable due to partially covalent bonding. Nonetheless, in other elements like fluorine, one can only find van der Waals forces.

The observation of supramolecular structures can be seen in the interlayer and intralayer distances between layers of diatomic molecules (Tab. 3). In elements that form supramolecular structures, we will see a decrease in the ratio of intralayer distance/diatomic bond distance, meaning they are more and more similar and therefore we are starting to see a supramolecular net.

The presence of only van der Waals forces generates low boiling and melting points and low vaporization energies, as we can see in table 4. In all of the mentioned values, we can observe some variations through the element group. This is due to the polarizability of the molecules. Some larger molecules like I_2 , in comparison with F_2 , have a more diffuse electronic density, which can make the van der

Halogen	X-X dist. (Å)	X-X interlayer (Å)	Ratio
Cl	1.98	3.32	1.68
Br	2.27	3.31	1.46
I	2.72	3.50	1.29

Tab. 3 Molecular and interlayer distances in halogens.

Waals forces stronger (strongly marked dipoles) and therefore increase the melting point, vaporization enthalpy, etc., since the structure is way harder to break.

	F ₂	Cl ₂	Br ₂	I ₂
PF (°C)	-223.10	-101.00	-7.25	113.60
PE (°C)	-188.10	-34.00	59.50	185.20
Radius (Å)	1.35	1.80	1.95	2.15
ΔH_{vap} . (kJ/mol)	6.54	20.41	29.56	41.95

Tab. 4 Halogen properties. PE stands for boiling point and PF stands for melting point.

4.1.1. Acidity

The H-F bond is found notably in hydrofluoric acid. We can compare hydrofluoric acid with other hydric acids. First of all, hydrofluoric acid has a higher boiling point than other acids. This is due to the very significant difference in electronegativity between fluorine and hydrogen : it's an extremely polar bond where the main interactions are electrostatic.

In addition, fluorine has three non-bonding doublets that form hydrogen bonds with other molecules in solution.¹²

The fluoridric acid is a weak acid. This could be explained by the free energy of the molecule in aqueous solution compared to the free energy of formation of the two ions H⁺ and F⁻. Thanks to the work done by Linus Pauling, we know that the free energy of formation for a given molecule is linked to the difference in electronegativity between the elements of the bond.

The more significant this difference in electronegativity, the greater the free energy of formation of the molecule, so it is more stable. We can compare these energies with the ones for other halogens in table 5.¹³

	$\Delta F^\circ(\text{H}^+ + \text{X}^-)$	$\Delta F^\circ(\text{HX})$
H-F	-66.08 (kcal/mol)	-70.41 (kcal/mol)
H-Cl	-31.35 (kcal/mol)	-22.8 (kcal/mol)
H-Br	-24.95 (kcal/mol)	-13.1 (kcal/mol)
H-I	-14.67 (kcal/mol)	-2.0 (kcal/mol)

Tab. 5 Standard Free Energies of Formation at 25°C of Hydrogen Ions Plus Halogenide Ions and of Hydrogen Halogenide Molecules in Aqueous Solution. Adapted from [13].

4.2. Fluorine : The Global Reactant

A rather surprising experimental fact is the dissolution of silicate glass by fluorine. Fluorine is particularly reactive

in the presence of silicon.

4.2.1. Use in Organic Chemistry

The stability of the Si-F bond compared with the Si-O bond largely explains this reactivity. There is a difference of 113 kJ/mol between the energy of the Si-F bond and the energy of the Si-O bond (Tab. 6), with the Si-F bond being the more stable.

This particular reactivity is often highlighted in organic chemistry.¹⁴ For example, when protecting ether alcohol groups in a multi-step synthesis, it is necessary to deprotect the alcohol at the end of the reaction.

With an ether function, the need to use expensive reagents (palladium) or hard synthesis conditions (use of very strong Brønsted acid) is a problem that needs to evolve in the context of green chemistry.

To partly solve this problem, the possibility of protecting an alcohol in the form of a silyl ether is a solution for deprotection under (generally) milder conditions and with less expensive reagents. The use of fluoride salts makes it possible to deprotect the alcohol, thanks to the stability of the Si-F bond compared with the Si-O bond.

Bond	Bond Energy (kJ/mol)
Si-O	452
Si-F	565

Tab. 6 Bond energies for Si-O and Si-F.

4.2.2. Glass Etching

Glass etching is also one of the areas where the reactivity between fluorine and silicon is highlighted. There are various methods, but acid etching is the most widespread.

This method involves bringing the glass into contact with hydrofluoric acid. The glass, composed of SiO₂, reacts with the fluorine in the following way¹⁵ :



This chemical reaction leads to the production of SiF₄ gas, which favors a direct reaction.

The advantage of hydrofluoric acid is that it can etch by attacking the surface of the glass layer by layer, enabling glassworkers to achieve etching results that would be impossible using other methods.

5. CONCLUSION

Silicon is one of the most widespread elements on Earth, and each of its forms has properties that enable it to be at the heart of many different applications. Silicates, the most common form of silicon, are found in glass, with a crystalline structure that gives it the piezoelectric properties we find in quartz watches.

Then there's metallic silicon, a semiconductor metal that doesn't exist in its native state and requires human intervention to come into being.

Silicon is highly reactive with fluorine, and this reactivity, used in organic chemistry for the protection and de-

protection of alcohol functions, led to the creation of gentler deprotection methods using fluoride salts. This reactivity is also used for etching silicate glass with HF, which is employed by many specialist craftsmen. However, it is important to look for new etching methods involving fluorine, but in the form of a less dangerous reagent than HF, to limit the risk of accidents.

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