5.2.2 Chemical Properties Relevant to Photovoltaics

Silicon is stable in the tetravalent state and has a strong affinity for oxygen, forming stable oxides and silicates, the only natural occurrences known for silicon. Artificially isolated elemental silicon immediately oxidises, forming a thin protective film of silica of less than 100 Å, which prevents further oxidation. Oxygen plays an important role in silicon-semiconductor devices, for instance, in manufacturing metal oxide semiconductor (MOS) transistors.

Silicon and carbon (Group IVA) form a strong Si–C bond and stable products. Silicon carbide is artificially synthesised in several allomorphic structures, finding various applications in photovoltaics and electronics. Primary uses are the abrasive properties of SiC for wafering silicon crystals and the emerging applications of SiC semiconductors. The strong Si–C bond is also the origin of the rich organosilicon chemistry encompassing numerous polysiloxanes (commonly named *silicones*) and organosilanes in which organic radicals are attached to silicon atoms through a covalent Si–C bond.

The tetravalence and the similarity of silicon and carbon are illustrated in the ability of silicon to form bonds with itself, Si−Si, and to form polymers, for example, $-(SiH_2)_p-$, $-(SiF_2)_p-$, comparable to hydrocarbons and fluorocarbons, although the length of the chains remains modest in the case of the silanes.

Silicon forms hydrides; Monosilane (SiH_4) is a key chemical compound for the production of amorphous silicon and the purification of silicon to semiconductor grade (see later in this chapter).

The chemical reactivity of silicon with chlorine is also extremely important. Alkyl- and arylchlorosilanes are the necessary intermediates to build the polysiloxane chains (silicones). Trichlorosilane and tetrachlorosilane, because they are volatile at low temperature and can be decomposed to elemental silicon at high temperature, are both the intermediates and the by-products of the purification processes upgrading metallurgical grade silicon to semiconductor purity (see later in this chapter). Other chlorosilanes or halogenosilanes are also used in chemical vapour deposition applications. The halogen atom is easily substituted by a hydroxyl group, −OH, through hydrolysis. Such a hydroxyl group tends to react with other functional groups by exchanging the hydrogen atom. This is the basis of a rich surface chemistry.

Silicon and germanium (Group IVA) are isomorphous and mutually soluble in all proportions.

Tin and lead, also elements of Group IVA, do not react with silicon and are not miscible in silicon, which is mentioned as a remarkable curiosity.

For more details on the chemical properties the reader is invited to consult the References [8–11].

5.2.3 Health Factors

The surface of elemental silicon is oxidised and is relatively inert and is considered as non-toxic. Hazard risks with elemental silicon are high when silicon occurs as a fine