5.6.3 Effect of Various Impurities

It is well known that impurity atoms have a strong effect on the efficiency of silicon as a photovoltaic material. It is also known that the effect of impurities can be changed by heat treatments and by exposing the material to gettering atmospheres in which selected elements diffuse into silicon and combine with the impurities (a semantic parallel to getter pumps in which oxygen is adsorbed by certain elements).

The impurity atoms may appear as solid solutions, as pairs with other elements, for example FeB, or as larger aggregates/precipitates with silicon and/or other elements, for example Fe_2Si. This depends upon the temperature, the concentration and the density of the imperfections (dislocations, grain boundaries). If the temperature or the (chemical) surroundings are altered, it will take some time before a new equilibrium is established. The time to reach equilibrium may depend on parameters such as temperature, cooling/heating rate, and chemical composition, grain size, dislocation density and others. When comparing results from literature values in which the specifications of relevant parameters are not defined, it is likely that differences may appear.

Most of the impurities in silicon used for PV cells exist at very low concentrations. Since measurements of trace quantities are difficult, much of the progress has occurred when new and better instrumentation has become available. Over the years many review articles and books dealing with the effect of impurities in crystalline silicon have been published. The interested reader is therefore encouraged to look up some of the references for a wider treatment of the subject [25, 28–33]. The following will therefore be an attempt to briefly summarise and update the general knowledge of the subject.

The maximum solid solubilities, $X_s(\max)$, of impurities in silicon are related to the distribution coefficients at the melting point according to an empirical relation found by Fischler [34]:

$$X_s(\max) = 0.1k_0$$

or in units of atoms/cm^3:

$$C(\max) = 5.2 \times 10^{21} k_0$$

Although deviations have been found for nitrogen, carbon and oxygen [35], the relation may be useful.

5.6.3.1 Atoms from Groups IIIA (B, Al, Ga...) or VA (N, P, As, Sb...)

These atoms act as substitutional impurities in silicon. At a site where a Group VA impurity (e.g. phosphorus) has replaced a silicon atom, four *d*-electrons are bound to the Si neighbours, while the fifth electron is weakly tied to the Group VA atom. The fifth electron is not completely free to move, but it is easily activated to the conduction band. Group VA atoms are therefore *donor* atoms.

In an analogous way, Group IIIA atoms (e.g. boron) do not have enough valence electrons to satisfy the four covalent neighbour bonds. This gives rise to holes weakly tied to the Group IIIA atoms. These impurities therefore create energy levels for electrons in the forbidden gap just above the valence band edge. Group IIIA atoms are called *acceptors*.