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Role of Impurities in Solar Silicon

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3.1 Introduction

Impurities in crystalline silicon can be classified into two categories, dopants and contaminants. Generally, dopants are intentionally added to modulate the resistivity, while contaminants are unintentionally incorporated during the material processing.

The quality of silicon depends on the purification processes associated with the manufacturing of the polysilicon feedstock starting from metallurgical silicon (see Chapter 2). However, during the entire manufacturing chain that leads to solar cells, both purification and contamination processes take place. In Section 3.2 the different sources of impurities and the related refinement processes are discussed. The impurity segregation mechanism during the crystallization of silicon ingots is reported in Section 3.3. In Section 3.4 the impact of metals, dopants and light elements on the solar-cell performance are discussed separately. The definition for solar silicon is discussed in Section 3.5.

3.2 Sources and Refinements of Impurities

Purity is one of the most important parameters used to describe the chemical quality of a material. Gold is generally thought to be one of the most pure materials. The purity of gold bars held in central bank reserves is of 99.99% purity (4N). However, silicon of this purity is considered ‘dirty’ for both microelectronic and photovoltaic applications.

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The main reason is that impurities in silicon cause a decreased carrier lifetime, which determines minority-carrier saturation currents in semiconductor devices and reduces the conversion efficiency in solar cells.

In Chapter 2 the technological processes developed and used today to purify silicon feedstock are described in details. In this chapter we consider where these impurities come from and how they are/could be removed and passivated.

Figure 3.1 illustrates the main sources of impurities along the overall production chain of crystalline silicon PV modules [1]. It is clear that impurities are introduced and removed during most of the steps of the production chain, as will be shown in detail, from the perspective of impurity sources and refinement.

The raw material used for the production of silicon feedstock is mainly quartzite and/or lumpy quartz. Depending on the location and geological characteristics of the mine, the impurities present can vary considerably. The main elements are usually iron, aluminum, titanium, calcium and cobalt. Dopant elements for silicon like boron and phosphorus are also present.

It is important to note that quartz is not the only source of impurities. An important additional source of impurities is, in fact, the carbon-based reducing agents used for the carbothermic production of silicon (coal, coke, charcoal or woodchips), which contain calcium, phosphorus, sulfur, and also metallic impurities in different amounts. The electrodes and the construction materials of the furnace itself introduce iron, chromium, nickel as well as other metals.

Silicon after the carbothermic process, has a purity of about 98% (1–2N) and the main impurities present are Fe, Al, Ca, Ti and C. The concentrations of Al, Ca and Mg can be significantly reduced during the tapping of the liquid silicon in large ladles by means of oxidation reactions and slagging. SiC is also removed from the liquid silicon during the slagging stage. The liquid silicon is then poured into a cast-iron molds where it solidifies. The solidified silicon is then crushed down. The crushers (jaws or rolls) contain, for example, molybdenum to improve their hardness, and therefore this step can also introduce unwanted contamination.

Silicon, at this stage, is called metallurgical grade (MG) silicon and requires additional purification to bring it to a purity greater than 6N, and hence be deemed usable for photovoltaic applications.

Since the aim here is to identify purification mechanisms and the sources of impurities, we categorize silicon feedstock production and purification in two different categories: synthesis of gaseous precursors (monosilane and chlorosilanes) and their gas-phase purification (which results in high-purity polysilicon) and liquid-phase purification of MG-Si. An extensive discussion on these technologies is given in Chapter 2.

Thanks to gas-phase purification, a silicon purity greater than 8N is achievable, which means a purification of more than 6 orders of magnitude with respect to MG-Si. Impurity contamination in this process might, however, occurs as a consequence of inefficiencies in the gas production processes or from the corrosion of materials in the reactors. For example Fe, Ni and Cr are typically observed in chemical vapor deposition (CVD) processes due to contamination from stainless steel parts of the reactors (Siemens process, see Chapter 2). Contamination from Cu might come from its use as a catalyst to increase the yield of the hydrochlorination reaction, for example in fluidized-bed reactor (FBR) processes, an alternative process developed to create polycrystalline granules and

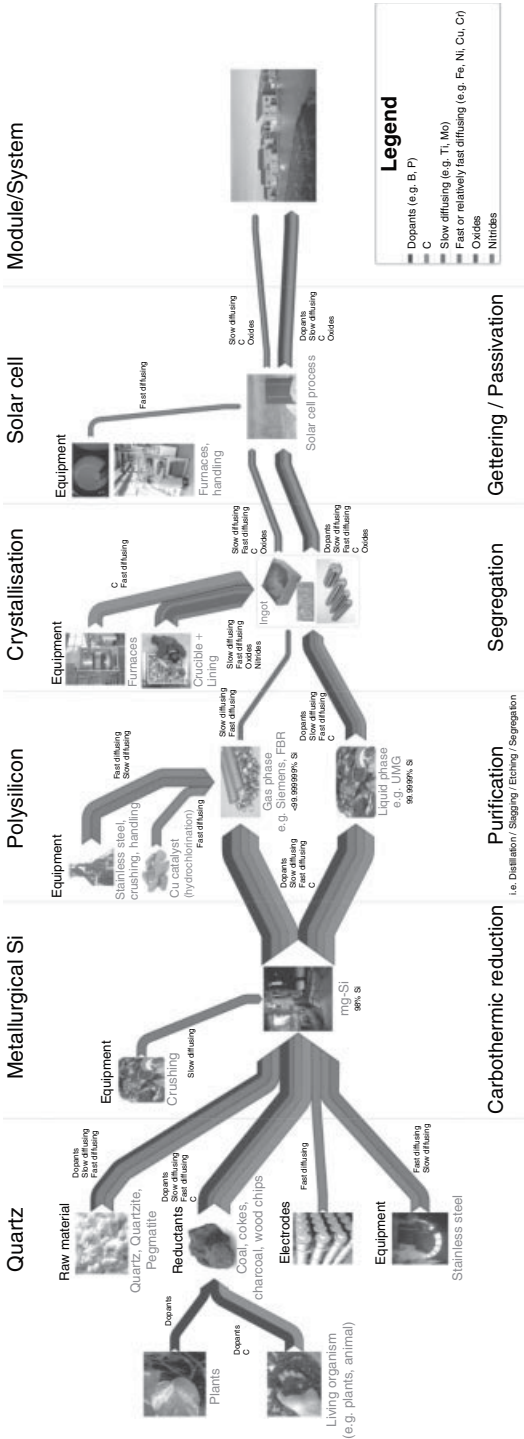


Figure 3.1 Impurity sources and refinement scheme. Reproduced from [1].

powders with reduced cost and environmental impact. Carbon contamination arises in the Siemens process due to the anchoring of the rods to the so-called ‘carbon ends’. In the traditional Siemens process, surface oxygen is of little concern due to the low surface-to-volume ratio of the rods. Instead, surface oxygen will be relevant for processes involving smaller particles, as the FBR processes, so powder/granular processes clearly present a challenge. In FBR processes, both hydrogen (when silane is used as precursor) and chlorine (when chlorosilanes are the feed gas) have been shown to be relevant due to phenomena sometimes called ‘popping’, involving particles exploding due to fast heating.

Handling and crushing of silicon rods, downstream from the gas-phase deposition, are sources of potential contamination. However, in general, gas-based chemical and CVD processes are suited to reach very low contamination levels, and are able to reach a purity as high as 10N [2].

Liquid-phase purification uses metallurgical processes, such as slagging, filtering, leaching, etching with a final stage consisting in a liquid/solid segregation (see Chapter 2) to purify MG-Si used as the raw material. It can reach purities of about 6N. This type of purification is, however, preferential for impurities having very small segregation coefficients (see Section 3.3), like most of the transition metals. Silicon dopant elements like boron and phosphorus are difficult to remove, using a sole liquid/solid segregation process, due to their segregation coefficients being close to unity. Aluminum is also difficult to remove due to its relatively large segregation coefficient. Its presence, or that of Zn, is systematic in feedstocks using Al or Zn as reducing agents for their purification. Carbon contamination is a direct consequence of the carbothermic reduction of quartz but also arises from the graphite parts in reactors used for the subsequent purification of MG silicon.

The development of purified MG-Si feedstock processes has increased considerably in the last few years, driven by the polysilicon feedstock shortage and the need for cost reductions. Transition-metal elements left in purified MG-Si are reduced considerably, reaching almost harmless levels, after the combined effects of segregation, gettering and possibly hydrogenation mechanisms that are carried out during solar-cell fabrication (e.g., solidification, emitter formation and hydrogen passivation). However, the presence of dopants, carbon and other inclusions, in the final ingots are a threat for this type of technology. In the following sections the effects of transition metals, dopants and light elements on solar-cell performance and their mitigation are discussed.

Crystalline silicon wafers are produced by slicing silicon ingots and used as substrates for solar-cell device fabrication. There are different crystallization techniques and methods available to produce ingots, or, in some cases, wafers directly. Typical examples are listed in Table 3.1. Each technique has different ways to melt the silicon, seed the crystallization and pull or cast the ingots. Consequently, the associated contamination is different, as is shown in Table 3.1 where the different sources of contamination are listed.

Note that the contamination sources in crystallization and wafering processes are not only related to the impurities present in the feedstock. Materials used for the equipment, like graphite heating elements in Czochralski and directional solidification furnaces, and consumables that are in direct contact with the silicon, such as quartz crucibles, are responsible for additional contamination. As an example, the main source of oxygen is the quartz crucible used for the growth of monocrystalline ingots due to the contact of

Table 3.1 Crystallization methods and contamination source.

Method	Crystallinity	Product	Contamination source	Contamination type
Czochralski	Monocrystalline	Ingots	Polysilicon Crucible Hot-zone parts	C, O, Al, transition metals
Float zone	Monocrystalline	Ingots	Feeding rod RF coil	Cu
Directional solidification	Multicrystalline	Ingots	Silicon feedstock Crucible Crucible coating layer Hot-zone parts	C, O, N, Al, transition metals
Ribbon	Multicrystalline	Wafers	Crucible, Mold Substrate Hot-zone parts	C, transition metals

the silicon with the crucible. This is also observed in multicrystalline ingots grown with the directional solidification technique due to inefficiencies in the coating with Si_3N_4 . The oxygen is dissolved in the silicon melt as SiO , due to a partial reduction of silica with silicon. Being very volatile, it sublimates from the liquid/gas phase interface,¹ but a small fraction remains in the liquid silicon and is then incorporated in the solid. During the solidification, however, the melt volume decreases due to the solidification and so the volume/surface ratio also decreases. Therefore, the concentration of SiO in the Si melt decreases due to sublimation and, as a consequence, the content of oxygen in the solid silicon decreases as well. The final oxygen profile in the ingot should depend, however, not only by the occurrences of this process, but also by the simultaneous process of oxygen segregation between the liquid and solid silicon phases. As the segregation coefficient of oxygen is about 1, the distribution of oxygen is dominated by the SiO sublimation process.

Also, nitrogen contamination occurs due to the contact of liquid silicon with the silicon nitride lining used for multicrystalline ingot production.

In case of transition metals and carbon, their distribution along the ingot is reversed. Most of the transition metals have such a small segregation coefficient that we can consider the amount of impurities actually depleted from the molten silicon interface to be negligible. At the same time the molten volume decreases as the crystallization proceeds. At 90% of the growth the molten volume is 10x smaller, which means, due to the negligible depletion, that a 10x higher concentration of impurities is present in the melt and therefore in the solid as well, in comparison to the initial concentration. At 99% of the growth the concentration is 100x higher and so forth.

Immediately after crystallization completion and during the cooling down process, the impurities, however, might diffuse back from the top, contaminating the ingot. This phenomenon is limited by the cooling rate and the impurity diffusion coefficients to a small fraction of the ingot height [3].

In addition, during the crystallization, the bottom and side parts of multicrystalline ingots are still at high temperature and are in direct contact with the crucible [4–7] and with the lining.

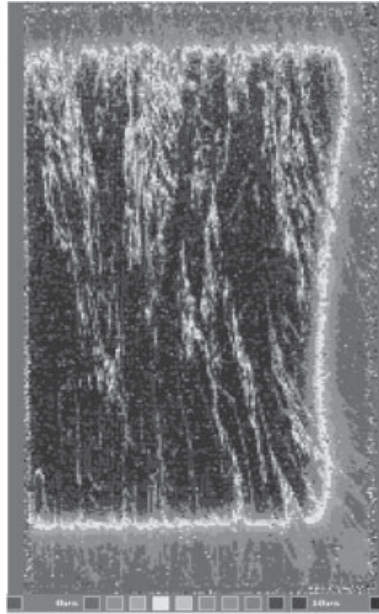


Figure 3.2 Lifetime map of a cross section of a multicrystalline ingot (courtesy of Photowatt Technologies).

Therefore impurities present in the lining, mainly the fast or relatively fast diffusers like Fe, can diffuse into the solid silicon [8].

Multicrystalline ingots typically show edge zones where this type of contamination is high, sometimes referred to as the ‘red zone’. This is visible in the lifetime map of the cross section of a multicrystalline ingot, as shown in Figure 3.2.

The side edges of any ingot show this impurity diffusion effect. The side ‘red zone’ is larger towards the bottom of the ingot showing a typical V shape. The bottom side part solidifies earlier, and therefore impurities have longer time to diffuse into the solid silicon than the top side, that solidifies later. The bottom part of ingots shows lower lifetimes that are the result of both solid-state impurity diffusion and the presence of extended defects. The lower lifetime in the top is mainly due to the segregation and back solid diffusion of metal impurities, as well as to the presence of precipitates and extended defects.

After the ingots have been produced they are cut into blocks and wafers with a typical size of $156 \times 156 \text{ mm}^2$. The consumables used for the squaring/blocking and wafering, such as slurries, SiC particles, as well as the wires and blades themselves, are sources of contamination that are not necessarily only superficial. Indeed the mechanical damage, even at a microscopic scale, can introduce impurities below the surface of the wafers. If these impurities are not thoroughly removed by proper etching procedures they can diffuse deep into the wafers during the following high-temperature processes, or contaminate the chemical baths employed in solar-cell manufacturing. The risk of chemical bath contamination is always present and sometimes neglected in PV processes. Impurities present on the wafer surface can contaminate the bath by

dissolution or etching. In turn, impurities in the bath with electronegativities higher than silicon segregate preferably on the silicon surface. Therefore, high importance should be given to the cleaning steps, cleaning of baths and of vessels, and the purity of the deionized water employed, in order to avoid replating effects and consequent bulk contamination during high-temperature processes.

After wafering and cleaning, saw damage is present at the wafer surfaces. A saw damage removal step is carried out as part of the solar-cell production, and contributes to the removal of residual surface contamination.

Impurity gettering and defect passivation take place during emitter formation and $\text{SiN}_x\text{:H}$ deposition and contact formation. Impurity gettering [9, 10] (see also Chapter 4) is a kind of solid/solid segregation process, caused by the higher solubility of impurities in the phosphorus (used as emitter in p-type wafers)-rich layer, which removes impurities from the wafer bulk. Fast and relatively fast diffusing impurities such as Fe, Cr, Cu and Ni can easily be gettered in this way. As reported in several studies [11, 12] the electronic properties of the silicon substrate improve dramatically after gettering, allowing the manufacture of very good solar cells out of wafers with very low initial minority-carrier lifetimes.

The overall effectiveness of phosphorus diffusion gettering is determined by a balance between impurity gettering and metal precipitates dissolution due to the high temperatures (above 800°C) involved [13]. Therefore degradation occurring by changing the impurity state into more detrimental and electrically active forms (e.g., dissolved impurities in their elemental state) can potentially overwhelm the positive effect of gettering. Crosscontamination from wafer to wafer, or from the furnace, can also take place during high-temperature processes.

Defect engineering aims to reduce the impact of impurities by manipulating their spatial distribution and chemical state without necessarily reducing their total concentration. Internal or relaxation gettering [14–17] consist of applying slow cooling rates or low temperature anneals to allow impurities to diffuse towards nucleation sites, where they can precipitate. In this way the concentration of impurities in the form of point defects is reduced [18].

High-temperature processes can cause precipitation of light elements such as C and O, as SiC or SiO_2 , which is often accompanied by the formation of extended defects (dislocations) and/or interaction with other impurities.

The hydrogenation [19] of defects takes place thanks to the passivation properties of hydrogen. This passivation is carried out during the metal contact formation due the hydrogen-rich SiN_x layer used as an antireflection coating.

Both gettering and hydrogenation mechanisms are extensively discussed in the next chapter.

In conclusion, the quartz employed is not the only impurity source, impurities are also introduced during the silicon refinement process and during the fabrication of ingots and solar cells. Therefore, refinement, removal and passivation mechanisms, occurring along the overall production chain, are crucial for the final performance of the solar cell. In particular, segregation during crystallization considerably reduces the concentration of transition metals, while the concentrations of fast and relatively fast diffusers are further reduced thanks to gettering. However, the impact of wafer gettering on residual slow diffusers such as Ti and Mo, which are also lifetime killers, is insignificant [20], due to the temperature and diffusion time typically in use during solar-cell processing. Bulk

dopant concentrations remain unaltered as well. C and O can change their state (for example by precipitation) during high-temperature processes, with various effects on the lifetime and on the solar-cell performance.

3.3 Segregation of Impurities During Silicon Growth

Crystallization is an integral part of the silicon purification process, since most impurities tend to segregate into the liquid during the growth, leaving the solid proportionally purer. The degree of purification for a specific impurity is given by its segregation coefficient. The segregation coefficient is usually smaller than 1, because impurity atoms have a smaller solubility in the solid silicon than in the liquid. An empirical correlation between the maximum solid solubility and the segregation coefficient was proposed by Fischler [21, 22] already in the 1960s. Since the solid solubility of impurities distributed in interstitial sites of the silicon lattice basically depends on their atomic size, their equilibrium segregation coefficients should also have a correlation with this. With an increase of impurity atomic size, the solubility in silicon usually decreases. Therefore, large impurity atoms are more difficult to incorporate into the silicon lattice, leading to small equilibrium segregation coefficients. In the case of iron, for example, the segregation coefficient is about 6×10^{-6} . In practice, the effective segregation coefficient is also affected by the diffusion coefficient of impurities in the melt and the physical conditions of crystal growth, in particular the extent of melt mixing and growth rate. As a result, during crystal growth impurities are mainly segregated along the growth direction, and are described by the normal freezing equation.

3.3.1 Equilibrium Segregation Coefficients

True equilibrium in a system means that the system is isothermal and that the impurity distributions in both the melt and crystal are uniform, without concentration gradients in either phase. In practice, the impurity distribution in the solid phase is not homogeneous, depending on crystal-growth conditions, since it takes a definite time for impurities to distribute themselves uniformly. Therefore, a true equilibrium state is practically impossible to achieve. Impurity segregation in silicon is conventionally described in terms of the ratio of impurity concentration in the solid and in the molten silicon, or by its equilibrium segregation coefficient, k_{eq} , defined as,

$$k_{eq} = \frac{c_S^I}{c_L^I} \quad (3.1)$$

where C_s is the impurity concentration in the crystal silicon at the crystal/melt interface, and C_L the impurity concentration in the molten silicon. At a thermal equilibrium state, the impurity concentrations in the solid and molten silicon can be obtained by the binary phase diagrams of impurity–silicon systems.

According to the phase diagram, the equilibrium segregation of impurities must be dependent on their solubility in silicon, and therefore, at least qualitatively, by their atomic sizes. Figure 3.3 shows the correlation of the equilibrium impurity segregation coefficients in silicon as a function of their atom sizes.

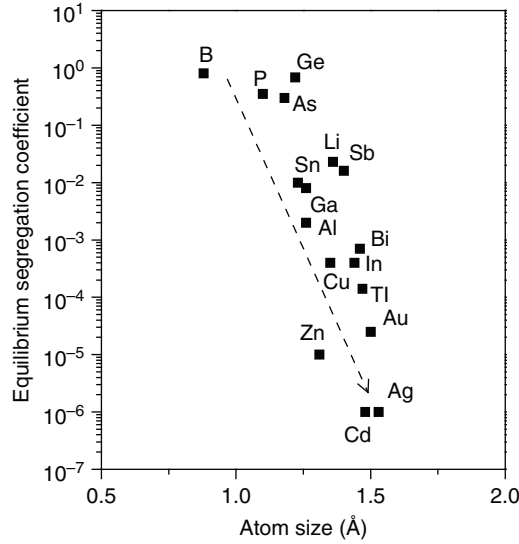


Figure 3.3 Equilibrium segregation coefficients in silicon versus the radius of impurity atoms.

3.3.2 Effective Segregation Coefficient

In practice, the impurity segregation during the growth of silicon crystals is influenced by many factors. Among them, the impurity diffusion at the crystal/melt interface plays an important role.

Thermodynamic equilibrium assumes complete mixing in the liquid. In the liquid the mixing is mainly driven by convection, which can be quite fast. However, a more realistic assumption is incomplete mixing in the liquid. Usually, an effective segregation coefficient (k_{eff}) is used to define the practical segregation behavior of impurities during silicon crystal growth. This effect was analysed by Burton, *et al.* [23] who suggested the presence of three different zones: a solid zone without diffusion, a static layer with thickness δ , where diffusion transport dominates, and a liquid zone with complete mixing and concentration C_L as described in Figure 3.4.

The diffusion zone, $0 < z < \delta$, is actually in a situation of steady-state diffusion, and the impurity concentration in the melt $C(z)$ can be obtained solving the one-dimensional diffusion equation giving

$$C(z) = B + (C_L^I - C_S^I) \exp\left(-\frac{\nu z}{D}\right) \quad (3.2)$$

where ν is the growth rate, D is the impurity diffusivity in the melt, B is a constant, C_L^I and C_S^I are the melt/solid concentrations at the interfaces.

At $z = \delta$, the impurity concentration in the diffusion zone is

$$C_L = B + (C_L^I - C_S^I) \exp\left(-\frac{\nu \delta}{D}\right) \quad (3.3)$$

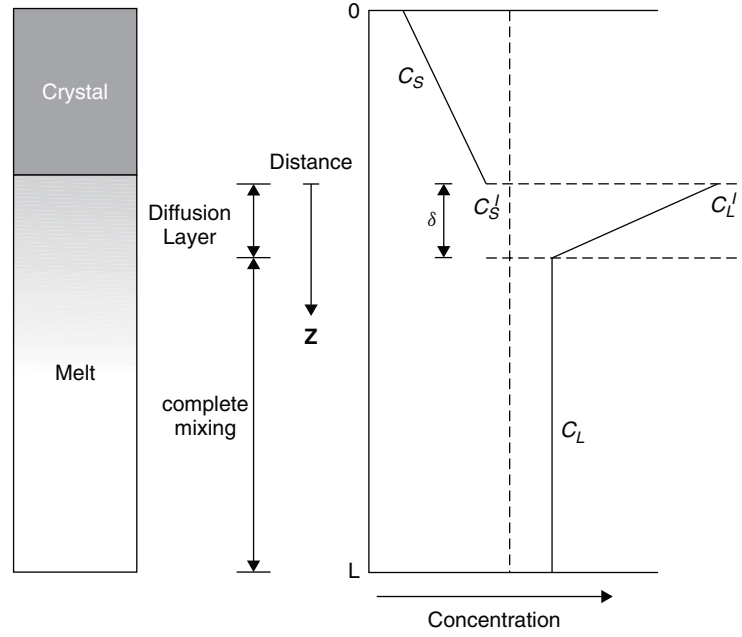


Figure 3.4 Schematic diagram of one-dimensional crystal growth, containing a boundary layer with thickness δ , and a region of complete mixing.

Using Equations (3.2) and (3.3), we can obtain

$$0 \leq z \leq \delta, \quad C(z) = C_L + (C_L^I - C_S^I) \left(\exp\left(-\frac{vz}{D}\right) - \exp\left(-\frac{v\delta}{D}\right) \right) \quad (3.4-a)$$

$$\delta \leq z \leq L, \quad C(z) = C_L \quad (3.4-b)$$

At the crystal/melt interface,

$$C_L^I = C_L + (C_L^I - C_S^I) \left(1 - \exp\left(-\frac{v\delta}{D}\right) \right) \quad (3.5)$$

Equation (3.5) can be changed into

$$1 = \frac{C_L}{C_S^I} - \left(\frac{C_L^I}{C_S^I} - 1 \right) \exp\left(-\frac{v\delta}{D}\right) \quad (3.6)$$

Note that if the effective segregation coefficient is defined as $k_{\text{eff}} = \frac{C_S^I}{C_L}$ and the equilibrium segregation coefficient is $k_{\text{eq}} = \frac{C_S^I}{C_L^I}$ then Equation (3.6) can be written as

$$k_{\text{eff}} = \frac{1}{1 + \left(\frac{1}{k_{\text{eq}}} - 1 \right) \exp\left(-\frac{v\delta}{D}\right)} \quad (3.7)$$

The value of k_{eff} depends strongly on δ . In practice, δ depends on the convection strength in the molten silicon and it is difficult to estimate. This means that there is no

simple way to predict k_{eff} . Note, however, that for $v\delta/D \ll 1$, i.e., for slow solidification and/or thorough stirring ($\delta \rightarrow 0$), Equation (3.7) reduces to $k_{\text{eff}} \cong k_{\text{eq}}$ and for $v\delta/D \gg 1$, i.e., fast solidification and/or no mixing ($\delta \rightarrow \infty$), Equation (3.7) reduces to $k_{\text{eff}} \cong 1$, implying full incorporation. From Equation (3.7), it can also be noted that with an increase of crystal growth rate, the value of k_{eff} increases.

Table 3.2 shows the effective segregation coefficients k_{eff} of various impurities in silicon.

Table 3.2 Effective segregation coefficients of main impurities in silicon [1].

Element	Method	Segregation coefficients			
		FZ		Cz	mc-Si
	Technique Reference Growth speed	k_{el} DLTS Lemke ^[24] 20 cm/h	k_{eff} NAA Coletti ^[20] ~9 cm/h	k_{eff} NAA Davis ^[25] 7 cm/h	k_{eff} NAA Coletti ^[26] ~1.5 cm/h
Dopants	Al			3×10^{-2} (2.8×10^{-3})	
	B			0.8	
	P			0.35	
Transition metals	Ag	5.0×10^{-7}			
	Au	5.0×10^{-5}			
	Co	1.0×10^{-7}		1.0×10^{-5}	
	Cr	2.5×10^{-6}		1.1×10^{-5}	3.1×10^{-6}
	Cu	3.0×10^{-7}		8.0×10^{-4}	
	Fe	5.0×10^{-6}	4.0×10^{-6}	6.4×10^{-6}	1.5×10^{-5}
	Hf	1.0×10^{-8}			
	Ir	1.6×10^{-6}			
	Mn	5.0×10^{-6}		1.3×10^{-5}	
	Mo	1.5×10^{-7}	2.0×10^{-7}	4.5×10^{-8}	
	Nb	1.0×10^{-7}		10^{-7}	
	Ni	1.5×10^{-7}		3.2×10^{-5}	8×10^{-4}
	Os	1.5×10^{-8}			
	Pd	1.6×10^{-6}			
	Pt	3.0×10^{-5}			
	Re	5.0×10^{-9}			
	Rh	1.8×10^{-6}			
	Ru	5.0×10^{-8}			
	Sc	1.8×10^{-7}			
	Ta	1.8×10^{-8}		2.1×10^{-8}	
	Ti	1.8×10^{-6}		2.0×10^{-6}	3.5×10^{-5}
	V	1.9×10^{-6}		4×10^{-6}	
	W	1.0×10^{-8}		1.7×10^{-8}	
	Zn			10^{-5}	
	Zr	1.8×10^{-8}		$<1.5 \times 10^{-7}$	
Other	C			0.05	
	Mg			3.2×10^{-6}	

Since the effective segregation is related to the particular growth conditions we have reported values determined in FZ, Cz and directionally solidified ingots. Values determined in experiments with FZ or Cz are usually assumed to approach equilibrium segregation coefficients.

The comprehensive work on segregation coefficients carried out by Lemke [24] on FZ silicon was based on deep level transient spectroscopy (DLTS) measurements, and therefore only accounts for the concentration of electrically active impurities (k_{el}). The work by Coletti *et al.* [20] determined the segregation coefficient also in FZ, but was based on neutron activation analysis (NAA) measurements, and was therefore sensitive to the total impurity concentration. In the cases of Fe and Mo the resulting k_{eff} are in excellent agreement with k_{el} . For other elements, like Cu, Ni or Co which diffuse and precipitate very quickly, the segregation coefficients k_{el} need to be corrected, taking into account the precipitation. Indeed by comparing the k_{el} values with k_{eff} data from Davis *et al.* [25] on Cz silicon calculated by NAA measurements, about 100–1000 times larger values are observed. The results for Fe reveal good agreement between k_{el} and k_{eff} in both FZ [20] and in Cz [25], which can be explained by the relatively low Fe diffusivity in comparison to the previously mentioned fast diffusers. Disagreement is found in the case of Mo between [20] and [25] where k_{eff} in Cz is about 1 order of magnitude smaller than in FZ, despite the similar growth speed and k_{el} being larger than k_{eff} . The case of Cr is peculiar in that Davis *et al.* measured a segregation coefficient about 1 order of magnitude larger than k_{el} , despite Cr precipitation being less likely than Cu and Fe, due to its smaller diffusivity (see Section 3.4 on the impact of transition metals). Coletti *et al.* [26] (Table 3.2) measured in mc-Si a segregation coefficient for Cr comparable to that of Lemke, therefore this value can be considered a more reliable upper limit for the segregation coefficient of Cr. We also have to consider that the disagreements are probably within the error of the measurement techniques used, and may also reflect differences in the conduction of the growth process. Values of k_{el} for Nb, Ta, Ti, V and W are in excellent agreement with k_{eff} from Davis. A separate discussion is needed for the results reported by Pizzini and Acciarri [27] on mc-Si. Both the data in [27] and [26] are based on mc-Si ingots and NAA but the results differ by several orders of magnitude (10–1000). Despite little information being available on the growth procedure in [27], we may expect that the large differences observed in the effective segregation coefficients for Cr, Ti, Fe and Ni are probably due to the particular growth conditions.

Note that among all the impurities, oxygen is the unique element that has a segregation coefficient [28] close or equal² to 1 (see Section 3.2 for details on oxygen distribution in silicon ingots). Furthermore, recent work has clarified that the segregation coefficient of germanium in silicon should be 0.56 [29], instead of 0.33, as was generally accepted.

3.3.3 Distribution of Impurities in Silicon Crystal Due to Segregation

During the crystallization an overall solute balance between the liquid silicon and the solid is established. This balance might be expressed in a differential equation that takes into account the characteristics of different crystallization techniques. In the case of Cz and directional solidification growths, the liquid volume decreases with the crystallization progress. The total amount of impurities in the crystal and in the melt should remain

constant, and can be written as,

$$\int_0^f C_S dx + (1-f)C_L = C_0 \quad (3.8)$$

where C_0 is the starting concentration of an impurity in the molten silicon, and f the solidified fraction. Converting the equation above by differentiating with respect to f , we can obtain

$$C_S + (1-f)\frac{dC_L}{df} - C_L = 0 \quad (3.9)$$

Considering $C_S = k_{\text{eff}}C_L$, Equation (3.9) becomes

$$\frac{dC_L}{C_L} = \frac{(1-k_{\text{eff}})}{(1-f)} df \quad (3.10)$$

By applying the boundary condition that $C_L = C_0$ at $f = 0$, Equation (3.10) can be solved as,

$$C_S = k_{\text{eff}}C_0(1-f)^{k_{\text{eff}}-1} \quad (3.11)$$

This expression is the so-called ‘normal freezing equation’ [30] describing the distribution of impurity concentrations along the axial direction.

Figure 3.5 shows the distribution of impurities along the axial direction of a silicon crystal for different values of k_{eff} . For $k_{\text{eff}} < 1$, the solidified crystal part contains fewer impurities. This will cause more and more impurities to remain in the melt, so the impurity concentration in the silicon melt increases with crystal growth. It should be noted that for $f \rightarrow 1$ the mass balance leads to nonphysical conditions since there are solubility issues (second-phase formation) which rule the maximum increase of the solid and liquid concentrations due to segregation. For $k_{\text{eff}} > 1$, the solid contains more impurities,

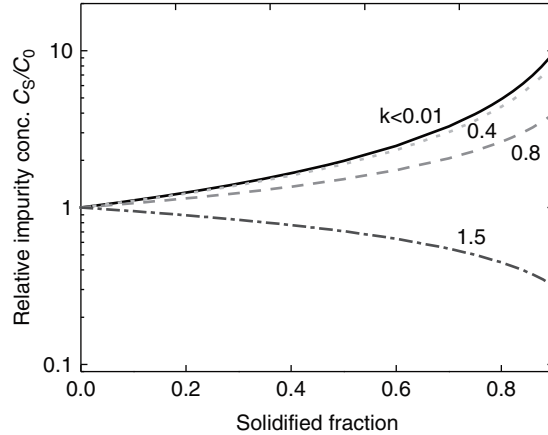


Figure 3.5 Distribution of impurities with different k values along the axial direction of a silicon ingot.

and the impurity concentration in the melt reduces with crystal growth, and goes to zero when f approaches 1.

In summary, the segregation coefficients in silicon are normally considerably less than unity, except in the case of oxygen, and generally decrease as the atomic size increases. In practical crystal growth conditions, effective segregation coefficients should normally be applied, whose values are influenced by the impurity diffusion in the melt, the boundary-layer thickness and the growth rate. The distribution of impurities in silicon crystals can be described by the normal freezing equation if the sublimation of the impurities from the melt and the melt or crystal contamination from other sources is negligibly small.

3.4 Role of Metallic Impurities

In this section we discuss the effect of metallic impurities on both the material and device properties. Impurities in silicon wafers are incorporated as foreign elements in the crystalline structure. They can be present as point defects, i.e., substitutional or interstitial in the lattice, as precipitates or at the surfaces of silicon wafers. Their chemical state and distribution depends mainly on the solubility and the diffusivity that are a specific characteristic of each element and essentially related to their atomic size and their affinity to form bonds with silicon atoms in the lattice. Impurities cause defect energy levels within the silicon bandgap, which increase recombination of charge carriers, and therefore strongly affect the electronic material properties. Last but not least, high-temperature processes change the state, aggregation and distribution of impurities. Therefore, the thermal history of ingots, wafers and solar cells determines the material properties under which the cells will operate.

3.4.1 Solubility and Diffusivity

The solubility of an impurity is defined as the maximum concentration that can be dissolved in the lattice at a given temperature. The solubility depends exponentially on the temperature according to the following (Arrhenius) equation

$$S = S_0 e^{-\frac{H_s}{kT}} \quad \text{for } T < T_{\text{eut}} \quad (3.12)$$

where H_s is the solution enthalpy, k the Boltzmann constant, S_0 is a temperature-independent pre-exponential factor and T_{eut} is the eutectic temperature. The solubility decreases drastically towards room temperature, therefore during cooling down processes (e.g., after ingot growth or emitter formation) the dissolved metals become increasingly supersaturated. To avoid supersaturation, which is a state with higher lattice free energy, impurities tend to form precipitates. However, for the precipitation to take place, a sufficient impurity concentration excess and diffusivity is required to form nuclei in the case of homogeneous precipitation. Once these nuclei are formed, or in the presence of heterogeneous nucleation points (e.g., other precipitates or crystallographic defects), an impurity should have sufficiently high mobility to diffuse towards the nucleation site and precipitate. The diffusivity also depends exponentially on the temperature, according to the following (Arrhenius) equation

$$D = D_0 e^{-\frac{H_m}{kT}} \quad (3.13)$$

where H_m is the migration enthalpy and D_0 is a temperature-independent pre-exponential factor. High diffusivity allows an impurity to move towards a region of higher solubility, for example to the phosphorus-rich layer, for segregation gettering, or towards the surfaces or nucleation sites, giving rise to relaxation gettering phenomena. In both cases, the driving force is a chemical potential gradient. Gettering effects are detailed in the next chapter.

Since each dissolved impurity can act as a recombination center, it would be preferable that impurities are agglomerated into precipitates or clusters in order to reduce the recombination activity per atom and therefore increase the minority carrier diffusion length. In general, the capture cross section of a precipitate is, among other things, a function of its size [13, 33, 34] and is therefore larger than the capture cross section of a single point defect. However, as precipitates are constituted of many single atoms, their impact on recombination is reduced in comparison to that of each single atom [33].

Figure 3.6 shows the solubility of the main impurities in silicon as a function of the diffusivity [34–35]. The ideal case for both relaxation and segregation gettering to occur is when the diffusivity is high enough to allow an impurity to diffuse in reasonable time, and the solubility is low enough to increase the gettering driving force. We distinguish between slow and fast diffusers, respectively, in the left and right side of Figure 3.6. For a target value of impurity concentration (equilibrium solubility) the graph shows the corresponding diffusivity. At 840°C, which is the typical temperature for phosphorus diffusion, the solubility of Ti is extremely low but its diffusivity does not allow enough mobility to reach the P-rich layer or other precipitation sites. On the other hand, in the case of Fe, Cr or even more Cu, the diffusivity is much higher, but a lower process temperature is needed in order to lower the solubility and benefit from a higher gettering effectiveness.

Slow diffusers like Ti, Mo and V are impurities whose presence/introduction into the silicon crystal should be avoided, since once they are incorporated in the ingot, they are

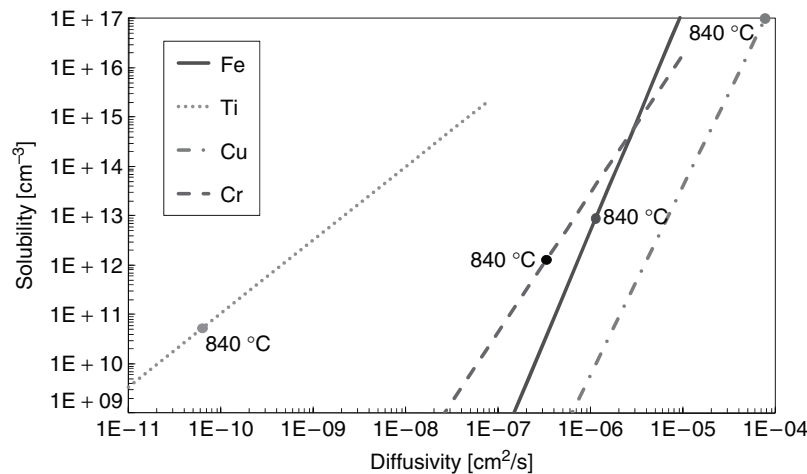


Figure 3.6 Solubility versus diffusivity for representative metals. The dots represent the solubility and diffusivity at 840°C, which is the typical temperature for P-diffusion [1].

very difficult to treat, being insensitive to any gettering process. Fast or relatively fast impurities like Cu and Fe are not so harmful even at relatively high concentration since they are getterable and therefore their impact on the material and solar-cell performance can be considerably reduced during solar-cell manufacturing. However in the presence of crystallographic defects (e.g., dislocations) the gettering effectiveness for such metals is strongly reduced [36, 37].

3.4.2 Impact on Charge-Carrier Recombination

The solar-cell conversion efficiency is directly related to its ability to collect and separate the electron–hole pairs formed by incident photons. Charge carriers recombining before they are collected do not contribute to the power output of the device, and therefore impact the conversion efficiency. Deep levels in the silicon bandgap, caused by defects and impurities, increase the recombination impact. Such defect-assisted recombination is referred to as Shockley–Read–Hall (SRH) [38, 39] recombination. The minority-carrier lifetime from the SRH theory can be written as:

$$\tau_{\text{SRH}} = \frac{\tau_{n0}(p_0 + p_1 + \Delta n) + \tau_{p0}(n_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} \quad (3.14)$$

where n_0 and p_0 are the equilibrium electron and hole concentrations, τ_{n0} and τ_{p0} are the lifetime constants for electrons and holes, related to the capture cross sections σ_n and σ_p , the thermal velocity v_{th} and the defect concentration N_t via $\tau_{n0}^{-1} = N_t v_{\text{th}} \sigma_n$ and $\tau_{p0}^{-1} = N_t v_{\text{th}} \sigma_p$. The parameters n_1 and p_1 are equal to the equilibrium electron and hole densities when the Fermi level is coincident with the defect energy level. We assume negligible carrier trapping, and so $\Delta n = \Delta p$.

The importance of this expression is that it allows modeling of the impact of the impurities on the lifetime, once the recombination parameters, defect concentration and operational injection level of the solar cell are known.

In Figure 3.7 the lifetime predicted by the SRH theory for several impurities is plotted as a function of their concentration. The lifetime is calculated at low injection level ($\Delta n \ll p_0, n_0, \Delta n \ll n_1$) for a p-type silicon with a bulk resistivity of $1 \Omega \text{ cm}$.

The lifetime at low-level injection is a reasonable approximation for typical solar-cell operation conditions, especially when multiple types of defects are present. Multiple defects may occur simultaneously, such as decorated grain boundaries or dislocations, or boron-oxygen complexes. The lifetime increases in inverse proportion to the defect concentration. In these conditions ($\Delta n \ll p_0, n_0, \Delta n \ll n_1$), the device lifetime in Equation (3.15) reduces to:

$$\tau_{\text{SRH}} = \tau_{n0} \left(1 + \frac{1}{p_0} \left(p_1 + \frac{\tau_{p0}}{\tau_{n0}} n_1 \right) \right) \quad (3.15)$$

At low defect concentrations this assumption is not necessarily satisfied, and therefore the injection level dependency of the SRH lifetime can play a role. In Figure 3.8 the lifetime as a function of the injection level for two different levels of interstitial Fe is shown for p-type and n-type silicon. For interstitial Fe in p-type silicon the injection level dependency is very steep (Figure 3.8 bottom graph) because the minority/majority capture cross section ratio is high ($\sigma_n/\sigma_p \sim 10^{-3}$). This means that by increasing the

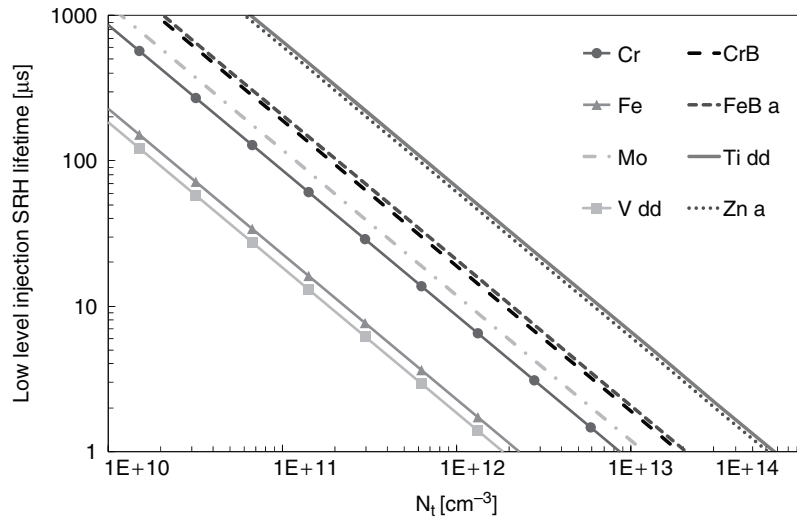


Figure 3.7 SRH lifetime of several impurities in Si as a function of defect concentration at low injection level for a bulk resistivity of $1\ \Omega\ \text{cm}$. In the legend a) means acceptor and dd) double donor [1].

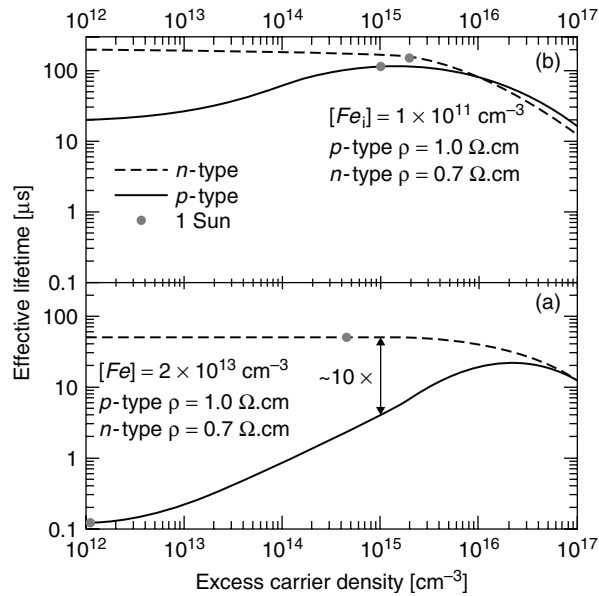


Figure 3.8 SRH lifetime of interstitial Fe as function of the injection level dependency. The lifetime corresponding to an illumination of 1 Sun is shown for two different Fe concentrations assuming no other defect in the bulk are present. The difference in p- and n-type is also shown. An emitter recombination current (J_{0e}) of $1 \times 10^{-13}\ \text{A/cm}^2$ has been used. The band to band and Auger recombination were considered. Reprinted with permission from [11]. Copyright (2008) American Institute of Physics.

injection level, the lifetime increases considerably. Since at low defect concentrations (Figure 3.8 p-type top graph) the injection level corresponding to 1 Sun is higher, a more rapid increase in the device operational lifetime is obtained than in the case of low injection level assumption. The bulk resistivity also strongly influences this effect. Lowering the dopant density lowers the excess carrier density corresponding to low injection levels, and therefore pushes the solar-cell operation condition towards higher injection and therefore higher lifetimes.

The minority/majority capture cross section ratio of other impurities like Cr is closer to unity: in this case, therefore, a higher operational injection level does not change significantly the figures in Figure 3.8.

Besides this, in Figure 3.7 it might be noted that the Ti double donor, a state that dominates in p-type silicon, is not actually such a strong lifetime killer as generally thought, since the corresponding lifetime is even higher than that of iron at the same defect concentration. Both Fe and Ti are lifetime killers, but Fe is very sensitive to gettering and therefore its concentration can be significantly reduced during cell processing, contrary to that of Ti.

In conclusion, to predict the impact of impurities on the solar-cell performance the amount of electrically active impurities (contributing to N_t) needs to be known (besides the impurity recombination parameters) and the precipitate size and distribution as well. This objective is quite ambitious and requires the setup of a dedicated experimental analysis that relates the initial impurity in the feedstock to the final solar-cell efficiency. Details concerned with this attempt are reported in the following section.

3.4.3 Modeling the Impact of Metallic Impurities on the Solar-Cell Performance

The minority-carrier diffusion length L_D is the key parameter describing the material quality and influencing as well the solar-cell performance. The (volume or bulk) diffusion length is calculated from the lifetime τ from the expression

$$L_D = \sqrt{D\tau}$$

where D is the minority carrier diffusivity. The performance of solar-cell devices can be calculated by numerical solution of the transport equations, with volume and surface recombination parameters as important inputs. Volume recombination is directly related to defect concentrations and activities and hence (among others) to metallic impurities. It is therefore possible to relate the efficiency to the diffusion length discussed in this section.

To model the effect of impurities one should know their recombination parameters and concentration in the device, as described in the previous section. Ample literature is available on recombination parameters for the main impurities, but there is not always agreement between data even for the most studied elements. In addition, recombination parameters of precipitates are not really known, hampering the modeling of impurities in a real situation where both dissolved and precipitated impurities are present. Therefore, more efforts are required in the determination of fundamental physical properties of impurities, especially in precipitated form.

Even more complex is the context when one has to predict behavior, state and distribution of impurities across the entire manufacturing process from ingot to module. Many models taking into consideration the impact of segregation and gettering have

been developed [13, 40]. However the difficulties are again in knowing the fundamental parameters that determine the physics. Additionally, experimental approaches require effort and are time consuming. Characterization of defects and parameter extractions often require microscopic analysis [41, 42] and extensive sample preparation that are not easily accessible.

The paramount work carried out in the 1970s and 1980s by Westinghouse within the “Low cost solar array” (LCSA) project is still used as a reference for the effect of impurities on solar-cell performance. This investigation, carried out mainly on Cz ingots, examined a very wide range of impurities. The main outcome of this work is a model that relates the concentration of impurities in silicon wafers, estimated from the effective segregation coefficient, with the solar-cell efficiency. However, because of numerous improvements and changes in cell processes since then, the increased use of directionally solidified multicrystalline ingots instead of single-crystalline ingots, more powerful computational tools and more accessible characterization facilities, there was a need for updated and more detailed studies [43]. Recently one of the present authors (G. Coletti) revisited the Westinghouse work, carrying out a systematic study on intentionally contaminated polysilicon and its effect on the solar-cell performance [20, 11, 27] within the European Integrated project CrystalClear [44] and the European project Foxy [45]. Among the most important differences between the investigation strategies are the facts that the present data refer to a modern, state-of-the-art industrial screen-print solar-cell process, and that the impact of impurities is investigated on directionally solidified multicrystalline ingots, as opposed to Czochralski silicon ingots. In this updated work the direct relationship between impurities in the feedstock and the final solar-cell performance is reported and discussed providing a straightforward and meaningful interpretation, especially in relation to specifying the feedstock impurity tolerances. The conclusions, therefore, do not rely on estimated segregation coefficients but uniquely on the added impurity concentration. In addition, the total ingot height, which corresponds to 100% of the melt weight, has been used for the evaluation, as opposed to one section analyzed in the LCSA project. Therefore, each ingot provides a broad range of impurity concentration levels of interest.

The model used takes into consideration the distribution of impurities along the ingot height and the impact of the diffusion-length reduction both in the bulk and in the emitter regions of the solar cell.

The impurity impact model was, in fact, developed to understand the main physical phenomena that contribute to the solar-cell performance degradation along the ingot. In addition, the model provides a mean to predict the behavior of solar cells manufactured from silicon containing known concentrations of impurities. The aim was also to define a unique parameter to quantify the ‘dangerousness’ of each impurity.

The model was based on the degradation due to the reduction in the base bulk lifetime for iron, chromium and titanium, while the emitter bulk recombination was taken into account to model the behavior of nickel. The combination of the two effects is considered to model copper.

The assumptions for the formulation of the model are listed below:

1. The impurity distribution along the ingot height scales according to the Scheil equation

$$C_s = k_{\text{eff}} C_0 (1 - x)^{(k_{\text{eff}} - 1)} \quad (3.16)$$

where C_s is the total concentration in the solid, C_0 is the starting concentration in molten silicon, k_{eff} is the effective segregation coefficient and x is the position from the bottom of the ingot.

2. The concentration of electrically active impurities (N_t) is proportional to the total concentration of impurities (C_s),

$$N_t = \alpha C_s \quad (3.17)$$

3. The minority-carrier lifetime (τ) in the base or in the emitter region can be described by:

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{imp}}} + \frac{1}{\tau_{\text{other}}} = v_{\text{th}} \sigma_{n,p} N_t + \frac{1}{\tau_{\text{other}}} \quad (3.18)$$

where $1/\tau_{\text{imp}}$ is a measure of the recombination due to the element intentionally added that is proportional to the concentration N_t of electrically active impurities at low injection level, and $1/\tau_{\text{other}}$ is a measure of the recombination due to other defects (i.e., not caused by the intentionally added impurity). v_{th} is the thermal velocity of the charge carriers and σ_n is the capture cross section of electrons for the respective metal.

4. The effect of impurities on the solar cell is that of increasing the recombination in the base or emitter region. The solar-cell performance as a function of the base and emitter bulk lifetime has been modeled using PC1D [46], software dedicated to the numerical solution of the transport equations.

More information about the model and the assumptions can be found in [27].

To extract the model parameters, the entire sets of data along the ingot heights have been used. This is necessary because it is of great importance to relate the impact of impurities to the usable fraction of the ingot, in order to gain insight into the contamination level allowed and their impact on the process yield.

The investigation was carried out by adding known amounts of impurities to high-purity virgin polycrystalline silicon. In order to keep the unintentional contamination to a minimum, a high-purity electronic grade quartz crucible and a purified Si_3N_4 lining were employed. The actual incorporation and segregation of impurities was determined by means of neutron activation analysis [8, 20].

Impurities like iron, chromium and titanium cause a reduction in the wafer minority-carrier diffusion length. However, the diffusion-length degradation alone cannot explain the solar-cell performance degradation. Indeed a poorer crystallographic structure has been reported [11] in ingots with high concentrations of iron, chromium, nickel and copper in comparison to reference uncontaminated ingots. Smaller grains and highly dislocated areas were found in the bottom and top of the ingots and do not seem to be related to the specific species added but rather to their concentration. Reference ingots show similar behavior only at the very top and bottom, showing that the effect on the contaminated ingots is due to the impurity interaction with the crystallization process. These extended defects are known to negatively influence the gettering effectiveness [36, 37] and therefore the impurity impact on the cell performance is heightened. Figure 3.9 shows the increase in extended defect density in an ingot contaminated with 50 ppm wt of iron in comparison to reference uncontaminated ingots.

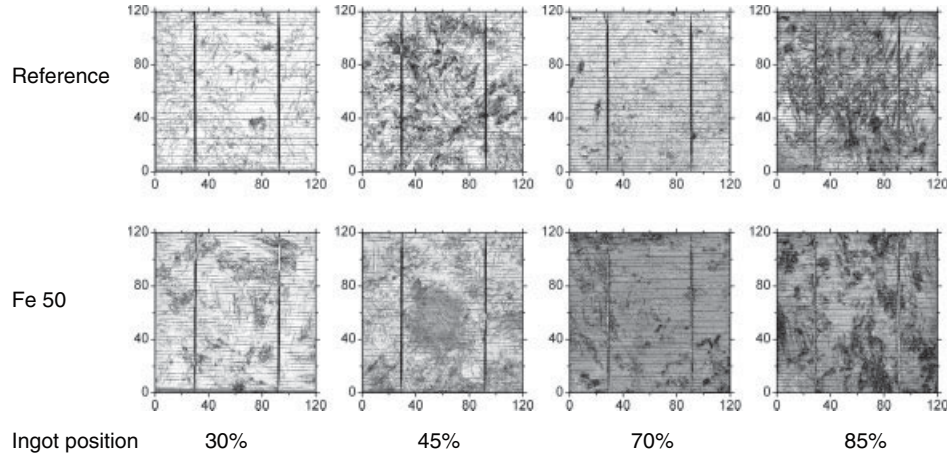


Figure 3.9 Diffusion length map of solar cells from an ingot contaminated with 50 ppm wt of iron and reference as a function of the ingot position. Reprinted with permission from [11]. Copyright (2008) American Institute of Physics.

Another type of interaction between impurities and crystallographic defects has been shown by Pizzini *et al.* [47] who reported a sensible increase in the recombination activity of GBs in the presence of high concentration of V, Ti or Cr. However, a redistribution of O between grain volume and GBs has been observed as a results of heat treatment, because of an influence of impurity–oxygen interaction on the phenomena cannot be excluded. For Fe [20, 47] and Mo [20] no clear increase in the recombination activity of crystallographic defects (GBs and dislocations) has been observed between intentionally contaminated and reference wafers.

On the contrary to Ti, Fe and Cr, the ingots grown with addition of nickel do not show any impact on the diffusion length, but a strong effect on the emitter recombination, reducing significantly the solar-cell performance. Copper, instead, has the peculiarity to impact both the bulk recombination as well as the emitter recombination.

The impact of the impurities on the fill factor (FF) cannot be modeled with a one-dimensional model since the FF is mainly limited by shunts that have a spatial distribution and involve interactions with other elements (e.g., nitrogen). Therefore we have chosen to model the $J_{sc} \times V_{oc}$ product of the solar cell along the ingot. The only fitting parameter of the model is the product $k_{eff} \times \sigma_n \times \alpha$. C_0 is the concentration of added impurity in the feedstock.

In Figure 3.10 is shown, as an example, the impact of 4, 40 and 200 ppm wt of Cr and 10 ppm wt of Ti added to the feedstock on the solar-cell performance along the ingots height. The larger impact of 10 ppm wt of Ti in comparison to 40 ppm wt of Cr is clearly visible. The model fits the experimental data trend very well along the ingot height with the exception of the bottom of the ingot (at higher impurity concentration) since the degradation in the bottom is not taken into consideration in the model.

The model parameters that fit the ingot with 40 ppm wt of Cr have been used to validate the model and to predict the degradation curve for the ingots with 4 and 200 ppm wt of Cr. The results in Figure 3.3 show that the model predicts very well the experimental data.

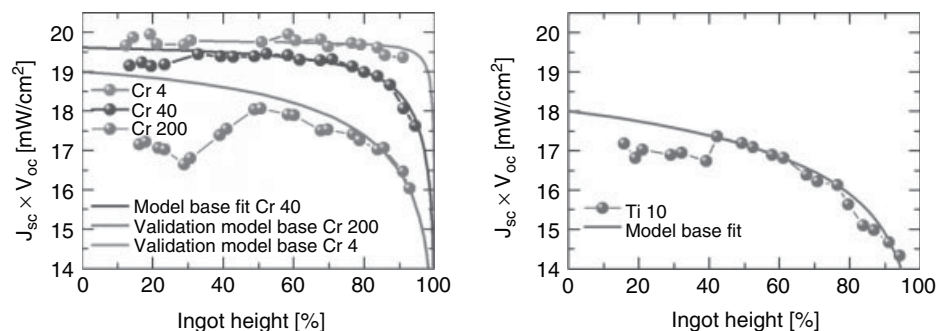


Figure 3.10 Impact of 4, 40 and 200 ppm wt of Cr (left) and 10 ppm wt of Ti (right) added to the feedstock on the solar cells performance along the ingots height. The fit to the data of the model employed and its validation for Cr are also shown. Reprinted with permission from [27]. Copyright (2011) Wiley-VCH.

The distribution of impurities according to the Scheil equation is the dominant mechanism explaining the solar-cell degradation along the ingot. The peculiarity of this finding is that the Scheil distribution leaves its fingerprint from the crystallization until the final solar cell. The effect of phosphorus gettering and hydrogenation reduces the impact of impurities, but the underlying trend from the Scheil equation remains. It is expected that the gettering flattens the distribution of impurity along the ingot. However, reduced gettering effectiveness has been reported towards the ingot top in the case of Fe, and this has been explained with the degeneration of the crystallographic structure (e.g., presence of GBs and highly dislocated areas) as reported in [11]. Indeed, the gettering effectiveness is known to be influenced by the presence of dislocations [36, 37].

This model is used to classify the dangerousness of each impurity and to estimate the impact of a certain amount of impurities in the feedstock on the solar-cell performance. C_L is defined as the limiting concentration of impurities in the liquid silicon charge which results in a relative performance degradation of about 2% up to 90% of the ingot height with respect to reference uncontaminated ingot. The meaning of C_L is that each single-impurity element, when present at this level, causes the same impact on the solar-cell performance distribution along the ingot. Each impurity has a characteristic value of C_L that therefore represents a true measure of the impurity impact. The higher the C_L value, the lower is the impact on solar cell level. Table 3.3 reports the model values of C_L .

One could note the relatively close levels of Cr and Fe. Cr has a diffusivity of about one order of magnitude smaller than Fe, therefore it is thought to be less sensitive to gettering. However, the effective segregation coefficient of Cr is one order of magnitude

Table 3.3 Impurity limit C_L corresponding to a performance degradation of about 2%_{rel} at 90% of the ingot height.

Impurity	Cr	Fe	Ti	Ni	Cu
Impurity limit C_L	8	11	0.11	13	8
[ppm wt] (ppma)	(4.3)	(5.5)	(0.065)	(6.2)	(3.5)

smaller than Fe, therefore for the same concentration of Fe and Cr in the melt, ten times more Cr segregates into the silicon melt, reducing the impact on the bulk. The tolerable level for Ti is 2 orders of magnitude smaller than Fe. This is directly related to the low diffusivity of Ti being four orders of magnitude smaller. Notable are the results for Ni and Cu, since both are believed to have a weaker impact on the cell performance than other impurities, mainly due to their large diffusivity. However, we need to consider that the segregation coefficient of copper is about two orders of magnitude larger than iron and Ni has a large impact on the emitter recombination.

Only if a single element is present and other sources of contamination (e.g., crucible, Si_3N_4 coating, etc.) provide a negligible contribution, C_L can roughly be approximated to the allowed concentration of impurities in the feedstock. Note that interactions between impurities can cause a nonlinear behavior, which complicates the estimate in the specific case.

It is important to note that C_L is not affected by the measurements of the effective segregation coefficient, the capture cross section and the electrical activity individually, since it is their product that is the fitting parameter in the model. Therefore, C_L directly relates the added concentration of impurities with the solar-cell performance, relying on the model assumptions alone.

The advantage of the model C_L value is that it includes all the different physical properties of a specific impurity (e.g., diffusivity, solubility, getterability, segregation coefficient, etc.) in one single parameter that is easy to compare.

3.5 Role of Dopants

A compensated semiconductor contains significant concentrations of both acceptors N_A and donors N_D . Silicon ingots made from ‘solar-grade’ feedstocks are often compensated due to the difficulty of removing dopants. A common metric for specifying the degree of compensation is the compensation ratio $R_C = (N_A + N_D)/|N_A - N_D|$, where the denominator is known as the net doping $p_0 = N_A - N_D$ in p-type material, or $n_0 = N_D - N_A$ in n-type material. This section examines the impact of compensation on the key electronic properties of silicon solar cells – namely carrier mobilities, recombination, and defect formation. These are important for evaluating the degree of compensation that is tolerable in solar cells. The positive effects of compensation on recombination are discussed, and the related concept of using deliberate compensation to make heavily doped feedstocks suitable for cell production, as well as the accompanying problems of nonuniform resistivity profiles along compensated ingots. Finally, some common experimental techniques for determining dopant concentrations in compensated silicon are summarized.

3.5.1 Carrier Mobilities in Compensated Silicon

Carrier mobilities are critical parameters for solar-cell performance, in particular the minority-carrier mobility, through its impact on the diffusion length, and hence on the collection efficiency at the cell junction. Several scattering mechanisms act to reduce the carrier mobilities in silicon – lattice scattering, carrier–carrier scattering, and scattering from ionized impurities (dopants). At room temperature, almost all boron and phosphorus dopant atoms are ionized, except in cases of very strong compensation. As a result,

there will be a greater concentration of ionized dopant atoms in compensated silicon compared to noncompensated silicon with the same free-carrier concentration, and this will naturally lead to a reduction in carrier mobilities.

Measurements of the conductivity mobilities (μ_C) in compensated p-type silicon, with N_A and N_D in the range 10^{16} – 10^{17} cm^{-3} and $R_C \sim 4$, have revealed a 15–20% reduction in the majority hole mobility, and around a 40% reduction in the minority electron mobility, compared to noncompensated samples with similar net doping [48]. In addition, there have been several reports of moderate reductions in the majority carrier Hall mobilities μ_H in compensated silicon [49, 50]. However, it is the conductivity mobility μ_C rather than the Hall mobility, which is relevant for solar cells. The Hall mobility and the conductivity mobility are related by the Hall factor r_H via $\mu_H = r_H \mu_C$. The Hall factor in compensated p-type silicon is similar to noncompensated silicon, with a value near 0.71 for low magnetic fields [48]. It is therefore reasonable to expect the Hall factor in compensated n-type silicon to be near 1.15, the value for noncompensated material [51].

In noncompensated silicon, resistivity ρ measurements correspond to the dopant concentration via $1/\rho = q\mu_p N_A$ (for p-type silicon). This calculation requires a suitable mobility model for μ_p , which is itself a function of N_A , and so an iterative approach is needed. However, in compensated wafers, the direct conversion from resistivity to net doping $p_0 = N_A - N_D$ (or n_0 in n-type material), via $1/\rho = q\mu_p(N_A - N_D)$, is in principle not possible without *a priori* knowledge of either N_A or N_D , since the mobility depends on both N_A and N_D (ionized dopant scattering), as well as $N_A - N_D$ (for carrier–carrier scattering). Methods for determining N_A and/or N_D in compensated silicon are discussed below. Alternatively, they may be estimated via segregation models if the dopant concentrations in the melt and the wafer position in the ingot are known. Note that it is only necessary to know the resistivity ρ and either N_A or N_D in order to iteratively determine the majority carrier mobility (via a suitable model) and the net doping.

There are numerous mobility models for crystalline silicon published in the literature. However, a model that independently accounts for scattering between holes and both donors and acceptors, and between electrons and donors and acceptors, as well as the standard carrier–carrier and lattice scattering, is in principle required to properly model mobilities in compensated silicon. An example of such a mobility model is Klaassen's model [52, 53]. However, there are few reports of comparisons between established mobility models and measured mobilities in compensated silicon.

Figure 3.11 shows the donor concentration dependence of carrier mobilities in compensated silicon predicted by Klaassen's model for a fixed acceptor concentration of $N_A = 5 \times 10^{16}$ cm^{-3} . As the donor concentration N_D increases, the material becomes more strongly compensated, resulting in an increase in resistivity (shown on the right-hand vertical scale). However, despite the decrease in free carriers, and the resulting decrease in carrier–carrier scattering, both the majority hole and minority electron mobilities, μ_p and μ_n , decrease slightly. This reveals that the additional scattering caused by the extra ionized donor atoms outweighs the reduction in scattering from fewer free carriers. As the concentration of added donors approaches $N_A = 5 \times 10^{16}$ cm^{-3} , the material becomes intrinsic, and then switches to n-type. As N_D increases further, the resistivity decreases rapidly as N_D dominates, and the mobilities decrease as they would in normal n-type silicon.

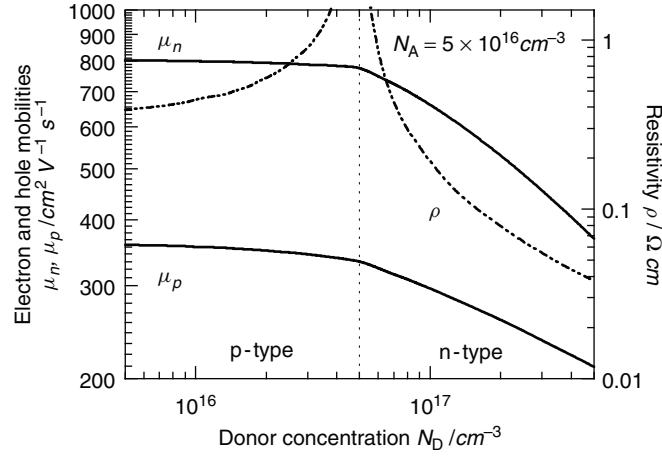


Figure 3.11 Electron and hole mobilities according to Klaassen's model for a fixed acceptor concentration N_A of $5 \times 10^{16} \text{ cm}^{-3}$, as a function of the compensating donor concentration N_D . The resistivity ρ is also shown on the right-hand axis.

3.5.2 Recombination in Compensated Silicon

Recombination of charge carriers in silicon solar cells is most often dominated by deep levels caused by defects and impurities, often referred to as Shockley–Read–Hall (SRH) recombination [40, 41]. The carrier lifetime τ_{SRH} resulting from SRH recombination can be written as:

$$\tau_{\text{SRH}} = \frac{\tau_{n0}(p_0 + p_1 + \Delta n) + \tau_{p0}(n_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} \quad (3.19)$$

where n_0 and p_0 are the equilibrium electron and hole concentrations, τ_{n0} and τ_{p0} are the capture time constants for electrons and holes, related to the capture cross sections σ_n and σ_p , the thermal velocity v_{th} and the recombination center concentration N via $\tau_{n0}^{-1} = Nv_{\text{th}}\sigma_n$ and $\tau_{p0}^{-1} = Nv_{\text{th}}\sigma_p$. The parameters n_1 and p_1 are, as usual, equal to the equilibrium electron and hole densities when the Fermi level is coincident with the recombination-center energy level. We have assumed there is negligible carrier trapping, and so $\Delta n = \Delta p$. The total carrier concentration is often written as $n = n_0 + \Delta n$ and $p = p_0 + \Delta p$.

Intrinsic recombination processes such as Auger and radiative recombination also occur in silicon, and are unavoidable, although they are often masked by SRH recombination. However, Auger recombination is important in heavily diffused regions, in the base when operating under strongly concentrated light, or in very high efficiency devices. The carrier lifetime resulting from intrinsic recombination in silicon, which is mostly dominated by Auger recombination, has been found experimentally to depend on the free-carrier concentrations as follows [54]:

$$\tau_{\text{Auger}} = \frac{\Delta n}{np(1.8 \times 10^{-24}n_0^{0.65} + 6 \times 10^{-25}p_0^{0.65} + 3 \times 10^{-27}\Delta n^{0.65} + 9.5 \times 10^{-15})} \quad (3.20)$$

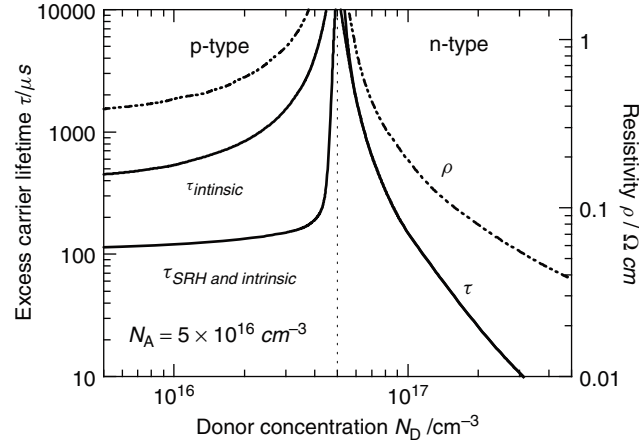


Figure 3.12 Intrinsic (low injection) and Shockley–Read–Hall (for interstitial Fe, 0.1 suns intensity) excess carrier lifetimes for a fixed acceptor concentration N_A of $5 \times 10^{16} \text{ cm}^{-3}$, as a function of the compensating donor concentration N_D . The resistivity ρ (dotted lines) values are reported on the right-hand axis.

The important point about both of these expressions, in the context of compensated silicon, is that it is the equilibrium free-carrier concentrations n_0 and p_0 that affect the lifetimes, rather than the dopant concentrations N_A and N_D .

The impact of compensation on the Auger lifetime is illustrated in Figure 3.12. In this plot, the acceptor concentration is fixed at $N_A = 5 \times 10^{16} \text{ cm}^{-3}$, and the concentration of compensating donor atoms increases along the horizontal axis, as in Figure 3.11. The resistivity is shown on the right-hand axis, calculated using Klaassen’s mobility model. The intrinsic Auger lifetime is calculated under very low injection conditions, where it is independent of the excess carrier concentration. Looking at the left-hand half of the plot, where the material is p-type, the positive effect of increasing compensation on the Auger lifetime is clear, and is a direct result of the reduced free-carrier concentration p_0 . As the material becomes strongly n-type doped in the right hand half of the plot, the intrinsic lifetime decreases rapidly, again in accordance with the free-carrier concentration n_0 .

Figure 3.12 also shows the impact of compensation on the SRH lifetime for the level associated with interstitial Fe. We have assumed an energy level of $E_V + 0.38 \text{ eV}$ [55], capture cross sections $\sigma_n = 1.3 \times 10^{-14}$ and $\sigma_p = 7 \times 10^{-17} \text{ cm}^2$ [55, 56], a thermal velocity of $v_{th} = 1.1 \times 10^7 \text{ cm/s}$ [57], and an interstitial iron concentration of $5 \times 10^{10} \text{ cm}^{-3}$. A carrier generation rate of 0.1 suns was used, in order to approximate maximum power conditions in a solar cell. The plotted values are actually the SRH lifetime combined with the Auger lifetime ($1/\tau_{\text{SRH and Auger}} = 1/\tau_{\text{SRH}} + 1/\tau_{\text{Auger}}$).

Again the positive effect of increasing compensation on the SRH lifetime is clear on the p-type side of the plot. As the material approaches the intrinsic point, the lifetime increases suddenly, by orders of magnitude, due to the reduced free-carrier concentration p_0 . The SRH lifetime then peaks at the ‘intrinsic’ point when $N_A = N_D$. Beyond this point, the material becomes n-type. Due to the large capture cross section asymmetry of interstitial Fe in silicon ($\sigma_n \gg \sigma_p$), the SRH lifetime in n-type silicon is much higher

than in p-type [58], and the global lifetime is then dominated by Auger recombination. Hence on the right-hand side of the plot, the $\tau_{\text{SRH, and, Auger}}$ lifetime coincides with τ_{Auger} .

The onset of this sudden lifetime increase on the p-type side is very close to the intrinsic point, meaning that strong compensation is required to achieve a large increase in lifetime in this case. However, the width and height of the region of increased lifetime depends strongly on the recombination parameters of the dominant recombination center, as well as the generation rate and the concentration of acceptors N_A . Lower values of N_A result in broader lifetime peaks for interstitial Fe, for example. Depending on their recombination parameters, a SRH level may result in no increase in lifetime with compensation, or may only have a positive impact in compensated p-type rather than n-type (as is true for interstitial Fe), or *vice versa*.

These examples serve to show that carrier lifetimes can, in principle, be increased by adding compensating dopants. This has been demonstrated experimentally in multicrystalline silicon [59], where the minority carrier diffusion length was found to double in the strongly compensated regions of a wafer. This would result in an improved cell current. However, since the cell voltage is proportional to $\ln(p_0 \Delta n / n_i^2)$ (for a p-type cell), significant improvements in the carrier lifetime are required to increase Δn (which is related to the lifetime via $\Delta n = G\tau$) enough to offset the reduction in p_0 , and thus maintain or improve cell voltage. To date, solar-cell results reported on compensated silicon have used solar-grade feedstocks that also contain other metal impurities, making the impact of compensation alone difficult to identify. Nevertheless, reported cell efficiencies have been very similar to standard noncompensated material, both for multicrystalline [60] and Czochralski-grown single-crystal [50] ingots, even near the top of the ingots where the compensation ratio became large ($R_C > 4$).

3.5.3 Dopant-Related Recombination Centers

Compensation can reduce the recombination activity of impurities in silicon by reducing the net doping. However, if the dopant atoms *themselves* form part of a recombination-active defect, the presence of additional dopant atoms could result in a greater concentration of defects, although their recombination activity will still be determined by the net doping. This could result in an overall reduction in the carrier lifetime. Perhaps the most important dopant-related defect in silicon solar cells is the well-known boron–oxygen defect [61]. These defects are prevalent in boron-doped p-type silicon containing significant quantities of oxygen, such as Czochralski-grown silicon, and to a lesser degree in multicrystalline silicon [62]. In noncompensated silicon, the defect concentration has been found to be linearly related to the boron concentration. Surprisingly, however, in compensated p-type silicon, it was found to be determined by the net doping, rather than the boron concentration [63], meaning that the additional boron in compensated silicon does not lead to a greater concentration of boron–oxygen defects.

Other dopant-related recombination centers that have been reported in silicon for solar cells are FeB and CrB pairs. However, in these cases, compensation is not expected to affect the concentration of the metal–dopant pairs, since this is determined solely by the concentrations of the metals, which are orders of magnitude lower than the dopant concentrations. Finally, compensated dopant atoms themselves have been proposed as possible recombination centers [59], although this remains experimentally unproven.

3.5.4 Segregation Effects During Ingot Growth

A major practical difficulty with using compensated silicon feedstocks is that the segregation coefficients of B and P are quite different, resulting in large variations in the net doping and resistivity of compensated silicon ingots. An example is shown in Figure 3.13, with initial dopant concentrations in the molten feedstock of $C_0 = 5 \times 10^{16} \text{ cm}^{-3}$ for B and $C_0 = 8 \times 10^{16} \text{ cm}^{-3}$ for P. The figure shows the modeled distributions of B and P along the ingot, as a function of the solidified fraction f_s . For a multicrystalline silicon ingot, the left-hand side corresponds to the bottom of the ingot, while for a Cz ingot, the left-hand side represents the top. The distributions are determined using the Scheil equation:

$$C_s = k_{\text{eff}} C_0 (1 - f_s)^{k_{\text{eff}} - 1} \quad (3.21)$$

where C_s represents the concentration in the solid at a certain solidified fraction, and k_{eff} is the effective segregation coefficient. Assuming that the solidification proceeds slowly enough and with sufficient melt stirring, the effective segregation coefficient k_{eff} should equal the equilibrium values of 0.35 for P and 0.8 for B. Values for some other common dopants are 0.008 for Ga, 0.0028 for Al, 0.023 for Sb and 0.3 for As [64].

Figure 3.13 shows the variation in the net doping, with a transition from p-type to n-type occurring when 55% of the charge is solidified. However, it has been realized [65, 66] that the addition of another p-type dopant with a segregation coefficient lower than P can result in a much more uniform net doping profile. An example is shown in Figure 3.14, which contains the same concentrations of B and P as Figure 3.13, but with an additional $1.05 \times 10^{18} \text{ cm}^{-3}$ of Ga in the starting melt. The resultant modeled net doping is almost uniform for more than 90% of the ingot height, and the material remains p-type along the entire length. Al also has a suitable segregation coefficient, but may have the disadvantage of promoting Al–O complexes, which can act as strong recombination centers [67].

Such ‘triple doping’ may therefore reduce the net doping variations in a compensated ingot, increasing the solar cell yield. However, the control of the dopant concentrations

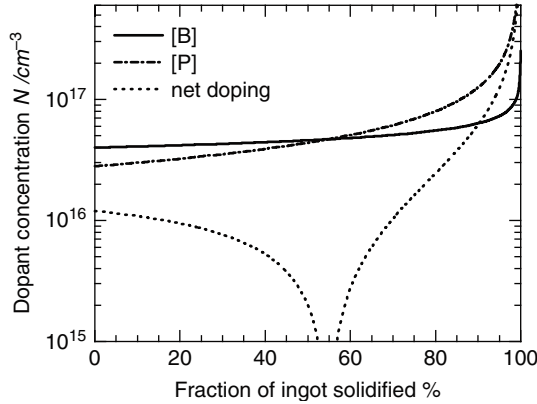


Figure 3.13 Modeled dopant concentrations for B, P and the net doping, as a function of the fraction of the ingot solidified. Initial melt dopant concentrations were $5 \times 10^{16} \text{ cm}^{-3}$ for B and $8 \times 10^{16} \text{ cm}^{-3}$ for P.

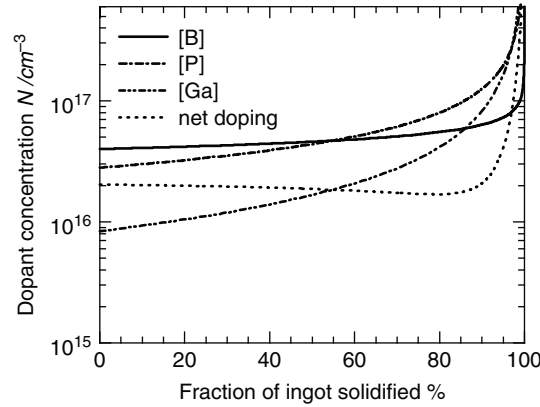


Figure 3.14 Modeled dopant concentrations for B, P, Ga and the net doping, as a function of the fraction of the ingot solidified. Initial melt dopant concentrations were $5 \times 10^{16} \text{ cm}^{-3}$ for B and $8 \times 10^{16} \text{ cm}^{-3}$ for Ga.

needs to be quite precise, which may be difficult in practice. Another important practical issue is how to monitor variations in unintended dopant concentrations in starting solar-grade feedstock, which determines the amount of compensating dopants to be added. Finally, it is worth noting that resistivities in standard noncompensated phosphorus-doped n-type ingots typically vary by about an order of magnitude. The addition of Ga to such ingots can dramatically reduce this variation.

3.5.5 Detecting Dopants in Compensated Silicon

Identifying dopant species and measuring dopant concentrations is important if compensated silicon is to be used for solar cells. Mass spectrometry (MS) methods such as secondary ion (SIMS), glow-discharge (GDMS) and inductively coupled plasma (ICP-MS) offer the advantage of identifying individual dopant species, and are quite robust. However, they detect the total dopant concentrations, not only the electrically active component. GDMS and ICP-MS are generally only sensitive above 10^{16} cm^{-3} , while the detection limit for SIMS can extend down to 10^{15} cm^{-3} in some cases. Details about these techniques are reported in Chapter 6 (Advanced analytical techniques for solar grade feedstocks).

Very low temperature ($<20 \text{ K}$) infrared absorption (FTIR) and photoluminescence (PL) spectra can be used to identify dopants and measure their concentrations [68, 69]. However, these techniques are only applicable for dopant concentrations below 10^{16} cm^{-3} , which is too low for most solar-grade silicon feedstocks. Low-temperature Hall measurements (between 77 K and room temperature) can also be used to identify and quantify dopants, based on the different ionizing temperatures of the various dopant species, and are suitable for dopant concentrations in the range 10^{15} – 10^{17} cm^{-3} [50]. Finally, the total acceptor concentration N_A can be determined by measuring the re-pairing rate of Fe–acceptor pairs after dissociation by illumination, using room-temperature carrier-lifetime measurements [70].

3.6 Role of Light Elements

3.6.1 Oxygen

Oxygen is one of the main impurities of Si crystals, which originates from the partial dissolution of silica crucibles, where Si crystals are grown, as well as from oxygen transport in the growth furnace [71]. As is known from the extremely vast literature on this subject, to which the interested reader is directed [70, 72–75], the elemental oxygen sits at the interstitial positions in the Si lattice, with the set-up of local strain conditions. The concentration of oxygen in Cz-Si and cast multicrystalline (mc-) Si is usually in the range of 10^{17} – $10^{18}/\text{cm}^3$. The diffusion processes of oxygen in Si are dominated by the structural configuration of oxygen in the Si lattice. In the temperature range 300–450°C and 700–1200°C, its diffusion might be described by an interstitial hop mechanism, where the hopping species is the interstitial oxygen (O_i). Instead, between 400°C and 700°C, oxygen has an anomalously faster diffusion rate, which has been explained by postulating the existence of a dimeric oxygen species O_{2i} . The interstitial oxygen atoms form covalent bonds with two neighbor Si atoms and therefore behave as electrically neutral species. However, it is also well known that oxygen in Si can form various defect complexes and microdefects, all of them having a detrimental influence on the performance of solar cells.

It is well known, as an example, that oxygen in Si can interact with boron to form a boron oxygen (B–O) complex, which causes an energy-conversion efficiency loss by 1–3% absolute under sunlight illumination, an effect commonly labeled as LID (light-induced degradation). The (B–O) defect concentration in Cz-Si has been experimentally demonstrated to be proportional to the total boron concentration and to the square of the oxygen concentration [70]. Accordingly, the chemical identity of this defect has been supposed to be the B_sO_{2i} complex, formed by the interaction of the fast-diffusing O_{2i} with the almost immobile substitutional boron ion B_s [70]. Recent results [76] however show that the (B–O) induced degradation in compensated Si should be explained by the formation of a B_iO_2 complex involving interstitial boron B_i , which better accounts for the dependence of the reciprocal lifetime on the uncompensated boron concentration.

Electrically charged, with a donor character, oxygen aggregates, conventionally labeled thermal donors (TDs), grow in the Si lattice by annealing Cz- or mc-Si samples in the temperature range 300–500°C. The generation of TDs will result in a resistivity decrease of n-type Cz or mc-Si and a resistivity increase of p-type Si samples, due to a charge compensation effect. In the limit case, an inversion of the conductivity from p-type to n-type could even occur. At 450°C, the TD concentration increases as a function of annealing time, see Figure 3.15, which shows that it can reach values close to $\sim 10^{15}/\text{cm}^3$ in the first 10 h. Obviously, such a high concentration of TDs would definitely affect the electrical performances of solar cells. So, an annealing process at temperatures larger than 600°C is needed to decompose TDs.

Since both Cz- and mc-Si crystals are supersaturated in oxygen, any kind of thermal annealing, also that occurring during the solidification of Si ingots, could cause the formation of TDs or oxygen precipitates. The presence of grown-in oxygen precipitates, whose amount depends on the thermal history of each ingot, is very important for the subsequent processing of Si crystals used for solar cells since they are associated with

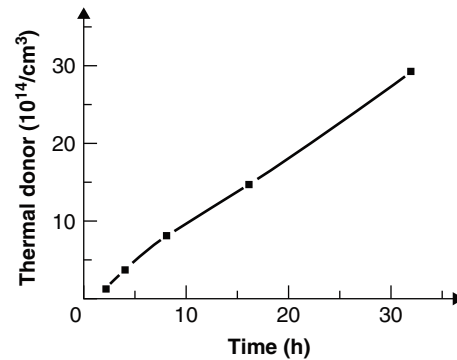


Figure 3.15 Thermal donor concentrations as a function of annealing time at 450°C.

deep energy levels in the bandgap, and therefore become recombination centers for minority carriers. The thermal history should be here understood as the *in situ* annealing of Si crystals after solidification. Voronkov and Falster [77] have proposed a model for the formation of grown-in oxygen precipitates in Cz-Si. Hwang and Schroder [78] have studied the recombination properties of oxygen-precipitated Si and found that the extent of lifetime degradation was more pronounced in p-type Si than in n-type Si. They proposed that the minority-carrier recombination at oxygen precipitates occurs thanks to their interface states. It is, however, possible that also the positive fixed charges in oxygen precipitates could be directly involved in the lifetime degradation of p-type Si.

For all these reasons, the oxygen concentration in Si crystals optimized for photovoltaic applications should be as low as possible.

3.6.2 Carbon

Carbon is often found as an impurity in Si crystals used for solar cells, in amounts depending on the growth technique and on the feedstock used. Also, a vast literature exists on carbon considering its close partnership with oxygen in heterogeneous processes involving the oxygen/carbon precipitation (see below) and the detrimental effects of SiC precipitates on solar-cell behaviors. In modern Cz-Si, the carbon is, however, generally below the detection limit of FTIR measurement. It is usually of the order of 10^{16} cm^{-3} , taking its lowest value at the seed-end part of crystal and then increasing along the axial direction of the crystal, thanks to its segregation coefficient that is about 7×10^{-2} , while the equilibrium solubility of carbon in liquid Si is $4 \times 10^{18} \text{ cm}^{-3}$ and that in Si crystal is $3.5 \times 10^{17} \text{ cm}^{-3}$ at the melting point. The situation is very different in mc-Si, where the average carbon concentration is in the order of 10^{17} cm^{-3} , due to a significant gas-phase (CO) carbon transport from the hot graphite parts of the growth furnace to the liquid Si and the general absence of gas shields in the growth furnace that would allow a better control of the dissolved carbon in the crystal. The distribution of carbon in the mc-Si blocks follows that in Cz-Si, with the lowest concentration at the bottom of block and the highest at the block's top, where SiC might precipitate from a supersaturated solution. The concentration of carbon in polycrystalline sheet and ribbon Si is even higher, in the range of 5×10^{17} – $2.5 \times 10^{18} \text{ cm}^{-3}$. Usually, carbon atoms in

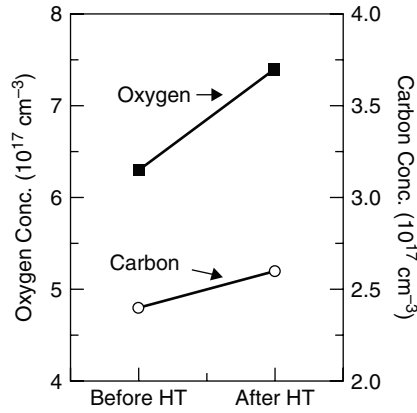


Figure 3.16 Substitutional carbon and interstitial oxygen concentrations of crystal silicon before and after 1260°C annealing.

crystalline Si sit in substitutional sites (C_s). Since the covalent carbon radius is much smaller than that of Si, near to substitutional carbon sites the lattice is under local strain. Although the substitutional carbon atoms have a low diffusion rate, they can easily jump to interstitial sites after capture a fast diffusing Si self-interstitial (I_{Si})



Carbon easily interacts with oxygen to form C–O complexes. It has been experimentally proven [79] that these complexes behave as the heterogeneous nucleation sites for oxygen precipitates during both crystal growth and following heat treatments. Figure 3.16 shows the substitutional carbon and interstitial oxygen concentrations of crystal Si before and after a 1260°C annealing. It can be seen that the carbon and oxygen concentrations simultaneously increase after the annealing, due to the dissolution of oxygen precipitates and decomposition of C–O complexes.

Carbon in supersaturated conditions should segregate in the form of SiC. Because of the large volume decrease associated with carbon precipitation and the relatively low diffusivity of C_s , carbon precipitation is difficult to proceed without the assistance of Si self-interstitials. However, as oxygen precipitation is associated with a volume increase and its strain relief occurs by punching out dislocation loops, or more probably, by emitting Si self-interstitials, the opposite volume change associated with oxygen and carbon precipitation favors their coprecipitation.

The substitutional carbon is electrically neutral, but the interstitial carbon maybe present in a negative, neutral or positive charge state, depending upon the position of the Fermi level. These carbon centers are highly mobile above room temperature and form complexes with the remaining substitutional carbon, oxygen, boron and various other impurity atoms. It has been reported [80] that wafers with higher concentration of C_s have a reduced minority-carrier lifetime degradation associated with the B–O complex formation respect to sample with similar B and O concentrations but low C_s as shown in Figure 3.17. The dissolved carbon might, therefore, have a strong influence on the photovoltaic properties of crystalline Si. It is found that the minority-carrier diffusion length,

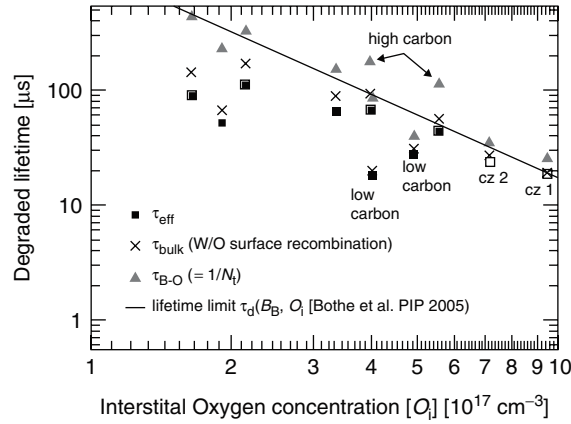


Figure 3.17 Degraded lifetime as a function of the interstitial oxygen concentration [90]. The solid line represents the degraded lifetime derived from the empirical equation as described by Bothe et al. [71]. The impact of carbon on the degraded lifetime is shown. Reproduced from [90].

the deep trap density and the solar-cell efficiency are, in fact, correlated with the carbon contents in Si [91]. Also the presence of SiC precipitates might cause severe drawbacks in solar-cell performance, associated with local ohmic shunts and short-circuit in the n^+ -emitter and in the back surface field [92], due to the high electronic conductivity of SiC. Four-probe measurements show, in addition, that SiC precipitates are often n-type and cause the setup of a local heterojunction at the Si/SiC interface, which behaves as a potential barrier for the majority carrier transport and a recombination center for minority carriers.

3.6.3 Nitrogen

Nitrogen is often introduced into Si crystal by gas dissolution or by partial decomposition of the Si_3N_4 coating layer on the inner wall of quartz crucibles used for mc-Si ingot casting. In equilibrium conditions it should sit in substitutional sites of Si lattice, with a solid solubility of about $4.5 \times 10^{15} \text{ cm}^{-3}$ at the Si melting point, whereas that in liquid Si is about $6 \times 10^{18} \text{ cm}^{-3}$. The diffusivity behavior of nitrogen in Si is still under debate. At the beginning, nitrogen had been considered for years as a slow diffuser like all substitutional impurities. Later, Itoh and Abe [93] found that the nitrogen pair has a very fast diffusion rate. As all the recent information on the nitrogen behavior in Si claims for high nitrogen diffusivity, the most stable nitrogen configuration in the Si lattice should be an interstitial pair. N–O complexes are thermally stable between 450 and 750°C and behave as shallow donors [94], therefore influencing the carrier concentration of Si crystals. Their formation is supposed to be associated with the interaction of N–N pairs with oxygen [95]. Their energy levels are 30–60 meV from valence or conduction bands. Figure 3.18 shows the carrier concentration of nitrogen-doped Cz-Si as a function of the annealing temperature and time [95]. It can be noted that the electrical activity of N–O complexes can be completely annihilated by a thermal treatment at 900°C for 90 min.

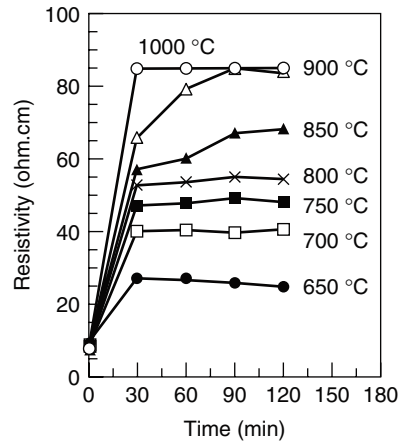


Figure 3.18 Carrier concentration of nitrogen-doped Cz silicon as a function of annealing temperature and time.

Nitrogen doping can improve the mechanical strength of Si [86]. This is assumed to be due either to the stronger capability of nitrogen, with respect than oxygen, to lock dislocations [87, 88] and/or to the nitrogen-induced enhancement of oxygen precipitates formation (see below), which could pin dislocations. The enhancement of mechanic strength of Si by nitrogen doping has been verified by experiments based on different techniques, including indentation and three-point bending methods. By indentation at room temperature followed by annealing at high temperatures, the dislocations in nitrogen-doped Si move much slower and propagate to a shorter distance than in nitrogen-free Si, due to a larger activation energy for dislocation displacement in nitrogen-doped Si [89]. Therefore, the warpage of Si wafers can be suppressed by nitrogen doping and the upper/lower yield points of Si wafers can also be enhanced.

Among other features, it must also be noted that nitrogen doping of float zone (FZ) Si can reduce both the interstitial (A-swirl) and vacancy-type defects (D-defects) content, as well as of that of the defects commonly labeled as COPs (crystal-originated particles). The concentration of nitrogen required for this effect is quite low, even smaller than 10^{14} cm^{-3} . Nitrogen doping of Cz-Si has a similar benefit, which is associated with the formation of $\text{N}_2\text{-V}_2$ or $\text{N}_2\text{-V}_2\text{-O}_x$ complexes at high temperatures [90]. It has been also experimentally demonstrated that nitrogen can affect the size and the density of voids in Cz-Si, favoring the creation of a greater number of smaller voids. The smaller defects are easier to anneal out, as can be seen in Figure 3.19 [91], and therefore are less likely to induce detrimental effects for photovoltaic devices [91].

As said before, nitrogen enhances the oxygen precipitation in Si, at high and low temperatures. In the first case the nucleation is associated with the presence of numerous heterogeneous nucleation sites, consisting of $\text{N}_2\text{V}_2\text{O}_x$ complexes. At low temperatures, N_mO_n complexes are, instead, the nuclei of small oxygen precipitates. As expected, the oxygen precipitation enhancement causes an average decrease of the minority-carrier lifetime in nitrogen-doped Si [92], as precipitates behave as recombination centers. In addition, the density of dislocations and stacking faults is also larger in nitrogen-doped

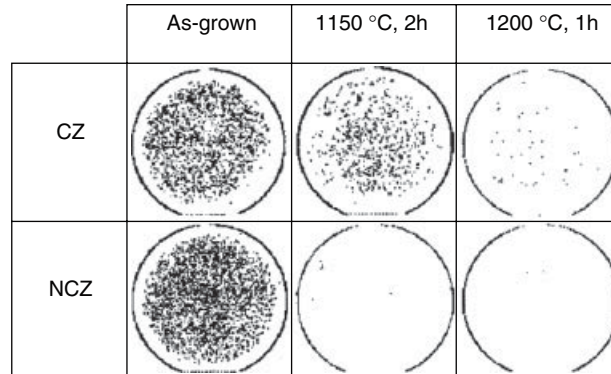


Figure 3.19 COPs on the conventional Cz and nitrogen-doped Cz silicon wafers after high-temperature annealing under H_2 atmosphere.

Si, both behaving as recombination and generation centers, when decorated by metals. When these defects occur in the active region of diodes, the leakage currents and the time of reverse recovery do increase considerably.

3.6.4 Germanium

Germanium (Ge), as a group IV element, is electrically neutral when present as a substitutional impurity in the Si lattice, nevertheless inducing considerable, local perturbation of the lattice that affects defect and impurity behavior. Mechanical strength improvement of Si crystals doped with Ge is considered to be effective for immobilizing and retarding the velocity of dislocations. Furthermore, dislocation-free Cz–Si crystal could be obtained using a heavily Ge-doped seed without Dash necking. Fukuda and Ohsawa [93] measured the mechanical strength of Si wafers by means of indentation tests, which are often employed as a simple method of assessing material strength. It could be experimentally proven that the mechanical strength of Cz crystals improves slightly as the Ge content increases from $6 \times 10^{19} \text{ cm}^{-3}$ to $6 \times 10^{20} \text{ cm}^{-3}$. The improvement of the strength of Ge-doped Cz crystals when the Ge concentration exceeds $6 \times 10^{19} \text{ cm}^{-3}$ is associated with the agglomeration of oxygen close to Ge atoms, which also lock dislocations.

Ge can also suppress the formation of TDs in Si. It has been, in fact, found that the rate of generation and the maximum concentration of TDs in Ge-doped Si are lower than those in conventional Cz–Si [94], see Figure 3.20. It is known that during the oxygen atom clustering to form TDs, lattice strain must be released by trapping free vacancies or ejecting interstitial Si atoms. However, in Ge-doped Si the larger covalent radius of Ge favors its interaction with vacancies to form Ge–V complexes and suppress the ejection of interstitial atoms, which may result in a retardation of TD formation.

Ge has a similar influence on oxygen precipitation and voids formation as nitrogen. It has been experimentally shown that in Ge-doped Si the nucleation of oxygen precipitates depends on not only the concentration of oxygen, but also the concentration of Ge [95]. It is well known that during the solidification of Ge-doped Cz–Si crystal, the substitutional Ge atoms will cause lattice distortion owing to their larger covalent radius compared

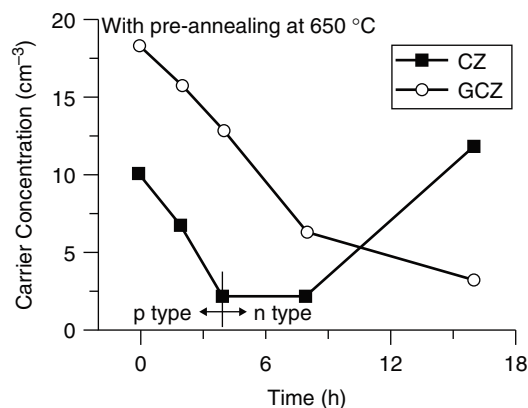


Figure 3.20 TD concentrations in the Cz and GCz wafers annealed at the temperature of 450°C with a preannealing of 650°C/1 h as a function of the annealing time.

with that of Si. Stress relief might be obtained by the interaction of Ge atoms with vacancies and interstitial oxygen to form (GeVO) complexes. The GeVO complexes can then become the nuclei of oxygen precipitates by trapping more oxygen atoms and also enhance the oxygen precipitation at high temperatures. An indirect effect of Ge doping is that the formation of (GeVO) complexes will consume a certain amount of vacancies and therefore reduce the total vacancies concentration available for the formation of voids. Thus, Ge doping can induce the formation of smaller voids, which can be easily eliminated at relatively low temperatures, as reported in [95, 96]. After vacancies are consumed by void formation, Ge atoms might directly bind oxygen to form Ge–O complexes. In subsequent annealing processes, Ge–O complexes can trap more oxygen atoms to form the nuclei of oxygen precipitates, thus providing the formation of small size oxygen precipitates.

3.7 Arriving at Solar-Grade Silicon Feedstock Definitions

In the past several years discussion has taken place on the specification for Solar Grade (SoG) silicon feedstock. The term SoG silicon feedstock dates back to the 1970s [97], which represent the early phase of the terrestrial use of photovoltaics following the oil crisis. It is meant to define the particular quality (‘grade’) of feedstock suitable for the PV industry, as distinguished from electronic grade (EG) feedstock suitable for the microelectronic industry. Today, however, almost 40 years later, there is still no final agreement on what this term should exactly identify and even less on the precise technical specifications. Few attempts have been made to define the specifications for SoG feedstock. Just to mention the most recent ones, in 2002 a workshop entitled “Silicon for a growing photovoltaic industry” [98] was held in the USA and it defined the specifications for one type of SoG feedstock based on total metal concentration, and B and P content for both p-type and n-type substrates. In 2008 within the European

Integrated Project “CrystalClear” a workshop [99, 100] entitled “Arriving to SoG silicon feedstock specification” was organized in Amsterdam on the 13th and 14th of November to discuss the same problem.

The most relevant aspect of a SoG feedstock, which resulted from the workshop discussion, is related to the allowed levels of dopants like B and P. Due to their high distribution coefficients their level cannot be lowered during the crystallization process. Furthermore, their removal during the silicon feedstock purification process is challenging for manufacturing technologies not relying on gas-phase purification (e.g., purified metallurgical grade (PMG), aka upgraded metallurgical grade (UMG) or direct route feedstock purification (DRP)). Compensation of P and B during the crystallization on the one hand and feedstock blending on the other hand are the most immediate way to deal with dopants. However, this approach is limited due to yield and resistivity issues (see section on compensation) as well as to the final feedstock cost. These are the reasons why the different feedstock categories are defined according to the concentration of doping elements: from undoped to heavily doped (see Table 3.4).

The next important aspect is the content of metallic impurities in the feedstock. Many studies report that, despite of the higher level of metal concentrations, similar solar-cell performance can be achieved to that obtained using electronic-grade purity feedstock [27, 101, 103]. The chemical and physical properties of the specific impurities are then crucial. Typical parameters are diffusivity and segregation coefficients, which differentiate the impact of each element. This leads to classes of metallic impurities: impurities with high diffusivity in silicon can be better tolerated than slowly diffusing ones, since they can be more easily manipulated during cell manufacturing by gettering processes.

Table 3.4 Solar-grade silicon feedstock categories.

Element	SoG category	SoG Undoped ppm wt	SoG Compensated ppm wt	SoG Heavily compensated ppm wt
B		<0.05	<0.45	–
P		<0.1	<0.6	–
Al		<0.05	<5	–
Fe		<0.05	<5	–
Cu		<0.01	<1	–
Ni		<0.01	<1	–
Cr		<0.05	<1	–
Ti and other slow diffusing		<0.005	<0.05	–
Na ^a			<0.008	
K ^a			<0.014	
Zn		–	<2	–
Ca		–	–	–
C		<5	<1 (Cz); <30 (DSS)	–
O		<5	<20	–
N		–	–	–

^aTo avoid crucible devitrification (very conservative)

A tentative and approximate standard set of specifications for solar-grade silicon suitable for the fabrication of solar cells, which resulted from the workshop discussion, is reported in Table 3.4. The feedstock is divided into three SoG categories according to dopants (B and P) content. Below we give a description of each category. The electronic-grade silicon as specified for the integrated circuits industry [103, 104], is considered a feedstock used for high efficiency ($>22\%$) cell designs only and is not included in the table.

Undoped SoG silicon: relaxed electronic-grade silicon, nominally uncompensated. This material is likely to come from a Siemens process or a fluidized-bed process. The Siemens process was designed to yield the purity and production rate set by semiconductor industry requirements, while capital expenditure and energy consumption were considered secondary criteria. For the PV industry a process with reduced cost, reduced energy consumption and increased production rates at the cost of purity levels is needed. This feedstock would be representative of new simplified production processes that have been (and are being) developed to serve the rapidly growing PV sector with its specific needs in a dedicated way. One way to do this is by relaxing the production procedures and quality control, which can lead to a cost reduction of approximately 35% [105]. Since the PV industry is much more sensitive to feedstock prices than the integrated circuit industry, it is anticipated that material from these techniques, which have been optimized in terms of costs and embedded energy for PV use, will become even more available.

For our purposes, we wish to specify a material that is perfectly suitable for all solar-cell designs and processes that will be in widespread use in the near future. This excludes the highest-efficiency cell designs ($>22\%$) that represent an important but relatively small fraction of total solar-cell production at present. Specifying a material that included these highest-efficiency cells would probably result in requirements very close to existing EG-silicon, overstating the requirements suitable for the vast majority of anticipated production.

Compensated SoG silicon: suitable for standard solar-cell processes and of sufficient quality for most future generations of higher-efficiency cells. This material is likely to come from one of the PMG (e.g., UMG) silicon routes. These methods consist of a sequence of improved carbothermic reduction of silica followed by leaching and directional solidification to reduce the content of metal impurities, and evaporation, purging, electrolysis and slagging to reduce the content of nonmetal impurities. The use of quartz and the reduction material is also investigated. The main consequence of these manufacturing techniques compared to Siemens or fluidized-bed feedstock is that there will be significant amounts of boron and phosphorus in the material together with other nonmetal elements (e.g., C and O). The goal of specifying this silicon is to enable the use of a feedstock material that could significantly affect the price, the environmental impact and the availability of silicon feedstock by accepting new manufacturing processes that could potentially be easier to quickly scale into mass production than the traditional polysilicon production. These specifications might also be broadly applied to other alternative sources of silicon such as tops and tails, discarded wafers, fines, and pot-scrap.

This material should be of a quality permitting the manufacturing of solar cells without significantly sacrificing efficiency (i.e., not more than a few tenths of an absolute per

cent). This new feedstock source should be nominally interchangeable with the feedstock in widespread use currently.

In addition, the presence of phosphorus in the material should typically not cause a yield in the directionally solidified silicon ingot that is lower than 95% in comparison to EG or undoped SoG feedstock. In compensated material, the top of the ingot generally cannot be used beyond the point of p- to n-type conversion. The preferred resistivity range of 0.5 to 5 ohm cm along with this 95% yield requirement poses a serious challenge for the commercial production of compensated material.

For some parameters, for example carbon content, it appears that a different specification should be made depending on whether the use is for Cz growth or directional solidification. For Cz, C is specified at 1 ppm wt, while 30 ppm wt is thought to be permissible for directional solidification.

Heavily compensated SoG silicon: suitable for standard solar-cell processes with significant process modification. Many scientific studies address the possibility to use feedstock with significantly relaxed specifications in combination with a cell process that is optimized *ad hoc* (i.e., specifically for that feedstock). Optimization could include defect-engineering techniques such as (wafer or cell) gettering, passivation through hydrogenation, and other techniques that effectively would allow to shifting of the last stage of feedstock purification to the wafer and cell-fabrication processes.

By opening the process tolerance window for silicon feedstock, it is anticipated that the silicon supply could be much larger and diverse at potentially lower cost and more environmental friendly, by using manufacturing techniques that are significantly altered from those typically used in industry currently.

This is a prospective material that requires successful development of advanced cell processing and crystallization techniques before it could be commercially significant. It is rather difficult to specify such a material with sufficient precision, because in this case also, a particular crystallization methodology and cell process might have to be specified as well. Some general guidelines can nevertheless be given:

1. This material can be considered for 'blending' with uncompensated feedstock, which add another free parameter.
2. The impurity concentrations must be low enough (limit on total concentration of metals) to permit good-quality crystallization because above a certain point the crystal quality will be lost. Gettering and defect passivation are much less effective if the crystal quality and structure are not good.
3. The metallic impurities can be classified. Fast-diffusing impurities can be better tolerated than slowly diffusing ones, since the fast diffusers can be more easily manipulated in the cell process by gettering. Specify total metal for 3 (or less) categories: fast diffusing (Cu, Ni, etc.), relatively fast (Fe, Cr, etc.) and slow (Ti, Mo, V, etc.). Al and Ti specifications should not be relaxed for this material because they are not getterable. Specifications for the fast and relatively fast impurities could be relaxed.

The general thought behind the categories proposed at the CrystalClear workshop in Amsterdam is that they allow correlation of feedstock properties with solar-cell performance. Such correlations hold *within* one category and, moreover, in relation to specific solar cell architectures and manufacturing processes.

Another method/approach to the specifications is, instead, to classify the different feedstocks according to the purification technology used. This has advantages for established and conventional technologies (i.e., conventional Siemens), however, it has disadvantages for new technologies that do not fit exactly within predetermined categories. Also, technologies (e.g., UMG) where feedstock characteristics are very broad from producer to producer will be penalized, for instance, many purification methods fall within the UMG label, however, dominant impurity content and feedstock purity differ considerably. The advantage of this approach is clearly that a more straightforward specification can be obtained but, on the other hand, the feedstock relationship to the solar-cell performance is not clear and therefore which solar-cell process would benefit from one or another technology.

The “CrystalClear” workshop on “SoG silicon feedstock specifications” also gave impetus to start an initiative [106] for the industrial standardization of silicon feedstock specifications via the institution of the “SEMI Standards PV Silicon Materials Task Force” [107] which published recently the first standard edition [108]. Another initiative to mention is the Chinese standardization process for polysilicon under AQSIQ [109]. Standardization has many advantages from an industrial development point of view, since it facilitates the communication and the procedures at the interfaces of customers and suppliers. In addition, standardization fosters industry growth and innovation. Therefore, these initiatives are very important for the further development of the sector.

For a standard to be effective it is important to define all the relevant parameters needed to be specified and, at the same time, to define measurement methods and sampling procedures that should be employed. This is the direction that the standardization initiative [108] by SEMI is heading in.

A detailed description of analytical techniques for impurities in silicon feedstock is reported in Chapter 6, together with updated references that can be found in [110]. Information on detection limits in silicon can be found in [110, 111].

In both specification approaches, by downstream application and by purification technology, the specification of each impurity or class of impurities do not cover the entire space of possible impacts. For example, defining the maximum level of slow diffusers like Ti and faster diffusers like Fe puts the specification on the safe side. In practice, when slow diffusers are not present, possibly higher levels of faster diffusers are allowed and *vice versa*. In this respect the impurity class should be defined among those impurities having similar effect on the solar-cell performance. The studies reported in Section 3.4 go in this direction, providing both the producer and user with information on the relative harmfulness of different impurities and therefore allowing comparison among their quantities.

More studies are required to reveal the relative impact of other elements than the ones studied and especially to understand the interactions between impurities and between impurities and crystallographic defects.

References

- [1] G. Coletti, (2011) Impurities in silicon and their impact on solar cell performance, <http://www.ecn.nl/nl/nieuws/item/date/2011/09/05/how-to-make-efficient-solar-cells-from-impure-materials/>, PhD thesis, Utrecht University, September 2011.

- [2] Wacker POLYSILICON, http://www.wacker.com/cms/media/en/publications/downloads/polysilicon_fifty.pdf.
- [3] D. Macdonald, A. Cuevas, A. Kinomura, Y. Nakano, and L. J. Geerligs, (2005) Transition-metal profiles in a multicrystalline silicon ingot *Journal of Applied Physics*, **97**, 033523.
- [4] T. Buonassisi, A. A. Istratov, M. D. Pickett, J. P. Rakotoniaina, O. Breitenstein, M. A. Marcus, S. M. Heald, and E. R. Weber, (2005) Transition metals in photovoltaic-grade ingot-cast multicrystalline silicon: Assessing the role of impurities in silicon nitride crucible lining material *Journal of Crystal Growth*, **287**, 402–407.
- [5] R. Kvannd, L. Arnberg, C. Martin, G. Rancoule, L. Dupuy, and A. Holt, in *Proceedings of the 21st EU-PVSEC*, 2006 (Dresden, Germany) 1052–1056.
- [6] B. Geyer, G. Schwichtenberg, and A. Muller, (2005) Increased wafer yield in silicon ingots by the application of high purity silicon nitride-coating and high purity crucibles in *Proceedings of the 31st IEEE PVSC*, 2005, Orlando, 1059–1061.
- [7] E. Olsen and E. J. Øvrelid, (2008) Silicon nitride coating and crucible – effects of using upgraded materials in the casting of multicrystalline silicon ingots *Progress in Photovoltaics*, **16**, 93–100.
- [8] R. Kvannd, L. J. Geerligs, G. Coletti, M. Di Sabatino, E. J. Øvrelid, and C. C. Swanson, (2008) Distribution of iron in multicrystalline silicon ingots *Journal of Applied Physics* **104**, 064905.
- [9] P. Manshanden and L. J. Geerligs, (2006) Improved phosphorous gettering of multicrystalline silicon *Solar Energy Materials & Solar Cells* **90**, 998–1012 and references therein.
- [10] A. Bentzen, A. Holt, R. Kopecek, G. Stokkan, J. S. Christensen, and B. G. Svensson, (2006) Gettering of transition metal impurities during phosphorus emitter diffusion in multicrystalline silicon solar cell processing *Journal of Applied Physics* **99**, 093509.
- [11] G. Coletti, R. Kvannd, V. D. Mihailitchi, L. J. Geerligs, L. Arnberg, and E. J. Øvrelid, (2008) Effect of iron in silicon feedstock on p- and n-type multicrystalline silicon solar cells *Journal of Applied Physics* **104**, 104913.
- [12] J. Tan, A. Cuevas, D. Macdonald, T. Trupke, R. Bardos, and K. Roth, (2008) On the electronic improvement of multi-crystalline silicon via gettering and hydrogenation *Progress in Photovoltaics: Research and Applications* **16**, 129–134.
- [13] P. S. Plekhanov, R. Gafiteanu, U. M. Gösele, and T. Y. Tan, (1999) Modeling of gettering of precipitated impurities from Si for carrier lifetime improvement in solar cell applications *Journal of Applied Physics* **86**, 2453–2458.
- [14] T. Buonassisi, A. A. Istratov, M. D. Pickett, and M. A. Marcus, (2006) Metal precipitation at grain boundaries in silicon: Dependence on grain boundary character and dislocation decoration *Applied Physics Letters* **89**, 042102.
- [15] J. Lu, M. Wagener, G. Rozgonyi, J. Rand, and R. Jonczyk, (2003) Effects of grain boundary on impurity gettering and oxygen precipitation in polycrystalline sheet silicon *Journal of Applied Physics* **94**, 140.
- [16] M. Rinio, M. Kaes, G. Hahn, and D. Borchert, (2006) Hydrogen passivation of extended defects in multicrystalline silicon solar cell in *Proceedings of the 21st EU-PVSEC*, (Dresden, Germany) 684–686.

- [17] W. B. Henley and A. Ramappa, (1997) Iron precipitation in float zone grown silicon *Journal of Applied Physics* **82**, 589.
- [18] A. A. Istratov, T. Buonassisi, R. J. McDonald, A. R. Smith, R. Schindler, J. A. Rand, J. P. Kalejs, and E. R. Weber, (2003) Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length *Journal of Applied Physics* **94**, 6552.
- [19] B. Sopori, Y. Zhang, and N. M. Ravindra, (2001) Silicon device processing in H-ambients: H-diffusion mechanisms and influence on electronic properties *Journal of Electronic Materials* **30**, 1616–1627.
- [20] G. Coletti, L. J. Geerligs, P. Manshanden, C. Swanson, S. Riepe, W. Warta, J. Arumughan, and R. Kopecek, (2008) Impact of iron and molybdenum in mono- and multicrystalline float-zone silicon solar cells *Solid State Phenomena* **131–133** 15–20.
- [21] S. Fischler, (1962) Correlation between maximum solid solubility and distribution coefficient for impurities in Ge and Si, *Journal of Applied Physics* **33**, 1615–1615.
- [22] F. A. Trumbore, (1960) Solid solubilities of impurity elements in germanium and silicon, *Bell Systems Technical Journal* **39**, 205–233.
- [23] J. A. Burton, R. C. Prim, and W. P. Slichter, (1953) The distribution of solute in crystals grown from the melt. Part I. Theoretical *Journal of Chemistry and Physics* **21** 1987.
- [24] H. Lemke, (1995) Substitutional transition metal defects in silicon grown-in by the float zone technique, *Material Science Forum*, **196–201** 683–688.
- [25] J. R. Davis, A. Rohatgi, R. H. Hopkins, P. D. Blais, P. Rai-Choudhury, J. R. McCormick, and H. C. Mollenkopf, (1980) Impurities in silicon solar cells *IEEE Transactions on Electronic Devices* **27**, 677–687.
- [26] G. Coletti, P. C. P. Bronsveld, G. Hahn, W. Warta, D. Macdonald, B. Ceccaroli, K. Wambach, N. Le Quang, and J. M. Fernandez, (2011) Impact of metal contamination in silicon solar cells, *Advanced Functional Materials* **21**, 5, 879–890.
- [27] S. B. S. Pizzini and M. Acciarri, (2005) From electronic grade to solar grade silicon: chances and challenges in photovoltaics *Physica Status Solidi A* **202**, 2928–2942.
- [28] B. Pajot (1999) in R. Hull. *Properties of Crystalline Silicon*, INSPEC, London, pp 484–487.
- [29] J. Chen, D. Yang, X. Ma, Z. Zeng, D. Tian, L. Li, D. Que, L. Gong (2008) Influence of germanium doping on the mechanical strength of Czochralski silicon wafers, *Journal of Applied Physics*, **103**, (12), 1–6.
- [30] M. C. Flemings (1974) *Solidification Processing*, Metallurgical and Materials Transactions B, **5**, 2121–2134, DOI: 10.1007/BF02643923. McGraw-Hill Inc, New York.
- [31] P. S. Plekhanov and T. Y. Tan, (2000) Schottky effect model of electrical activity of metallic precipitates in silicon, *Applied Physics Letters* **76**, 3777–3779.
- [32] H. Hieslmair, A. A. Istratov, T. Heiser, and E. R. Weber, (1998) Evaluation of precipitate densities and capture radii from the analysis of precipitation kinetics, *Journal of Applied Physics* **84**, 713–717.
- [33] A. A. Istratov, T. Buonassisi, R. J. McDonald, A. R. Smith, R. Schindler, J. A. Rand, J. P. Kalejs, and E. R. Weber, (2003) Metal content of multicrystalline

- silicon for solar cells and its impact on minority carrier diffusion length, *Journal of Applied Physics* **94**, 6552–6559.
- [34] K. Graff, (1999) *Metal Impurities in Silicon-Device Fabrication*, 2nd edn, Springer, Berlin, Vol. 24.
- [35] A. A. Istratov, H. Hieslmaier, and E. R. Weber, (2000) *Iron contamination in silicon technology*, *Applied Physics A* **70**, 489–534.
- [36] B. Sopori, (2002) Silicon solar cell processing for minimizing the influence of impurities and defects, *Journal of Electronic Materials* **31**, 972–980.
- [37] O. Schultz, S. W. Glunz, S. Riepe, and G. P. Willeke, (2006) High-efficiency solar cells on phosphorus gettered multicrystalline silicon substrates, *Progress in Photovoltaics* **14**, 711–719.
- [38] W. Shockley and W. T. Read, (1952) Statistics of the recombinations of holes and electrons *Physical Review* **87** 835–842.
- [39] R. N. Hall, (1952) Electron-hole recombination in germanium *Physical Review* **87**, 387.
- [40] J. Hofstetter, J. F. Lelièvre, C. del Canizo, and A. Luque, (2009) Acceptable contamination levels in solar grade silicon: From feedstock to solar cell, *Materials Science and Engineering B*, **159–160**, 299–304.
- [41] T. Buonassisi, A. A. Istratov, M. A. Marcus, B. Lai, Z. Cai, S. M. Heald, and E. R. Weber, (2005) Engineering metal-impurity nanodefects for low-cost solar cells, *Nature Materials*, **4**, 676–679.
- [42] H. Nordmark, M. Di Sabatino, M. Acciarri, J. Libal, S. Binetti, E. J. Øvrelid, J. C. Walmsley, and R. Holmestad, (2008) EBIC, EBSD and TEM study of grain boundaries in multicrystalline silicon cast from metallurgical feedstock, *Proceedings of the 33rd IEEE Conference*, San Diego, USA, 1–6.
- [43] L. J. Geerligs, P. Manshanden, G. P. Wyers, E. J. Øvrelid, O. S. Raanes, A. N. Waernes, and B. Wiersma, (2005) *Proceedings of the 20th EU-PVSEC* (Barcelona, Spain) 2005, pp. 619–712.
- [44] *CrystalClear Integrated Project* (SES6-CT_2003-502583).
- [45] *Foxy – Development of solar-grade silicon feedstock for crystalline wafers and cells by purification and crystallisation* (SES6-019811).
- [46] P. A. Basore, (1990) Numerical modeling of textured silicon solar cells using PC-1D, *IEEE Transactions on Electron Devices*, **37**, 337–343.
- [47] S. Pizzini, L. Bigoni, M. Beghi, and C. Chemelli, (1986) On the effect of impurities on the photovoltaic behaviour of solar grade silicon. II. The influence of titanium, vanadium, chromium, iron and zirconium on PV behaviour of polycrystalline solar cells *Journal of the Electrochemical Society* **133**, 2363–2373.
- [48] F. E. Rougieux, D. Macdonald, A. Cuevas, S. Ruffell, J. Schmidt, B. Lim, and A. Knights, (2010) Electron and hole mobility reduction and Hall factor in phosphorus-compensated p-type silicon, *Journal of Applied Physics* **108** 13706–13710.
- [49] S. Pizzini and C. Calligarich, (1984) On the effect of impurities on the photovoltaic behaviour of solar-grade silicon, *Journal of the Electrochemical Society* **131**, 2128–2132.
- [50] J. Libal, S. Novaglia, M. Acciarri, S. Binetti, R. Petres, J. Arumughan, R. Kopecek, and A. Prokopenko, (2008) Effect of compensation and of metallic impurities

- on the electrical properties of Cz-grown solar grade silicon, *Journal of Applied Physics* **104**, 104507.
- [51] F. J. Morin and J. P. Maita, (1954) Electrical properties of silicon containing arsenic and boron, *Physical Review* **96**, 28–35.
 - [52] D. B. M. Klaassen, (1992) A unified mobility model for device simulation – I. Model equations and concentration dependence, *Solid-State Electronics* **35**, 953–959.
 - [53] D. B. M. Klaassen, (1992) A unified mobility model for device simulation – II. Temperature dependence of carrier mobility and lifetime, *Solid-State Electronics* **35**, 961–967.
 - [54] M. J. Kerr and A. Cuevas, (2002) General parameterization of Auger recombination in crystalline silicon, *Journal of Applied Physics* **91**, 2473.
 - [55] A. A. Istratov, H. Hieslmair, and E. R. Weber, (1999) Iron and its complexes in silicon, *Applied Physics A* **69**, 13–44.
 - [56] D. Macdonald, J. Tan, and T. Trupke, (2008) Imaging interstitial iron concentrations in boron-doped crystalline silicon using photoluminescence, *Journal of Applied Physics* **103**, 073710.
 - [57] W. M. Bullis and H. R. Huff, (1996) Interpretation of carrier recombination lifetime and diffusion length measurements in silicon, *Journal of the Electrochemical Society* **143**, 1399.
 - [58] D. Macdonald and L. J. Geerligs, (2004) Recombination activity of iron and other transition metal point defects in n- and p-type crystalline silicon, *Applied Physics Letters* **85**, 4061.
 - [59] S. Dubois, N. Enjalbert, and J. P. Garandet, (2008) Effects of the compensation level on the carrier lifetime of crystalline silicon, *Applied Physics Letters* **93**, 032114.
 - [60] C. Modanese, M. D. Sabatino, A.-K. Sjøiland, K. Peter, and L. Arnberg, (2011) Investigation of bulk and solar cell properties of ingots cast from compensated solar grade silicon, *Progress in Photovoltaics: Research and Applications* **19**, 45–53.
 - [61] J. Schmidt and K. Bothe, (2004) Structure and transformation of the metastable boron- and oxygen-related defect center in crystalline silicon, *Physical Review B* **69**, 024107.
 - [62] K. Bothe, R. Sinton, and J. Schmidt, (2005) Fundamental boron-oxygen-related carrier lifetime limit in mono- and multicrystalline silicon, *Progress in Photovoltaics: Research and Applications* **13**, 287.
 - [63] D. Macdonald, F. Rougieux, A. Cuevas, B. Lim, J. Schmidt, M. DiSabatino, and L. J. Geerligs, (2009) Light-induced boron-oxygen defect generation in compensated p-type Czochralski silicon, *Journal of Applied Physics* **105**, 093704.
 - [64] J. D. Plummer, M. D. Deal, and P. G. Griffin, (2000) *Silicon VLSI Technology – Fundamentals, Practice and Modelling*, Prentice Hall, Upper Saddle River, New Jersey.
 - [65] C. Bucher, D. L. Meier, D. Leblanc, and R. Boisvert, (2008) Method for utilizing heavily doped silicon feedstock to produce substrates for photovoltaic applications by dopant compensation during crystal growth, International patent WO 2008/112598 A2.

- [66] J. Kraiem, R. Einhaus, and H. Lauvray, (2009) Doping engineering as a method to increase the performance of purified MG silicon during ingot crystallisation, in *Proceedings of the 34th IEEE Photovoltaic Specialists Conference*, Philadelphia (IEEE New York, 2009), p. 1327.
- [67] J. Schmidt, (2003) Temperature- and injection-dependent lifetime spectroscopy for the characterization of defect centers in semiconductors, *Applied Physics Letters* **82**, 2178.
- [68] *Semi Standard MF1389-0704*, (2004) Test methods for photoluminescence analysis of single crystal silicon for III-V impurities.
- [69] *Semi Standard MF1630-1107*, (2007) Test method for low temperature FT-IR analysis of single crystal silicon for III-V impurities.
- [70] D. Macdonald, A. Cuevas, and L. J. Geerligs, (2008) Measuring dopant concentrations in compensated p-type crystalline silicon via iron-acceptor pairing, *Applied Physics Letters* **92**, 202119.
- [71] K. Kakimoto, A. Tashiro, T. Shinozaki, H. Ishii, and Y. Hashimoto (2002) Mechanisms of heat and oxygen transfer in silicon melt in an electromagnetic Czochralski system, *Journal of Crystal Growth* **243**, 55–65.
- [72] J. C. Mikkelsen, S. J. Perton, J. W. Corbett, and S. J. Pennycook (1986) Oxygen, carbon, hydrogen and nitrogen in crystalline silicon *Proceedings of the MRS Symposia*, Boston, Massachusetts, USA, **59**.
- [73] R. Hull (1999) *Properties of Crystalline Silicon*, INSPEC, London.
- [74] W. C. O'Mara, R. B. Herring, and L. P. Hunt (1990) *Handbook of Semiconductor Silicon Technology* Noyes Publications, Park ridge, NJ, USA.
- [75] F. Shimura, (1994) *Oxygen in Silicon, Semiconductors and Semimetals*, Vol. **42**, Academic Press, Boston, Massachusetts, USA.
- [76] V. V. Voronkov and R. Falster, (2010) Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells *Journal of Applied Physics* **107**, 053509.
- [77] V. V. Voronkov and R. Falster, (1998) Vacancy-type microdefect formation in Czochralski silicon, *Journal of Crystal Growth* **194**, 76–88.
- [78] J. M. Hwang and D. K. Schroder, (1986) Recombination properties of oxygen-precipitated silicon *Journal of Applied Physics* **59**, 2476–2487.
- [79] D. Yang and H. J. Moeller, (2002) Effect of heat treatment on carbon in multicrystalline silicon, *Solar Energy Material & Solar Cells*, **72**, 541–549.
- [80] G. Coletti, C. L. Mulder, G. Galbiati, and L. J. Geerligs, (2006) Reduced effect of B-O degradation on multicrystalline silicon wafers, *Proceedings of the 21st EU-PVSEC* (Dresden, Germany) 1515–1518.
- [81] J. Bauer, O. Breitenstein, and J. P. Rakotoniaina, (2007) Electronic activity of SiC precipitates in multicrystalline solar silicon, *Physica Status Solidi A* **204**, 2190–2195.
- [82] O. Breitenstein, J. P. Rakotoniaina, M. H. Al Rifai, and M. Werner, (2004) Shunt types in crystalline silicon solar cells, *Progress in Photovoltaics: Research Applications* **12**, 529–538.
- [83] T. Itoh and T. Abe, (1988) Diffusion coefficient of a pair of nitrogen atoms in float-zone silicon, *Applied Physics Letters* **53**, 39–41.

- [84] V. V. Voronkov, M. Porrini, P. Collareta, M. G. Pretto, R. Scala, R. Falster, G. I. Voronkova, A. V. Batunina, V. N. Golovina, L. V. Arapkina, A. S. Guliaeva, and M. G. Milvidski (2001) Shallow thermal donors in nitrogen-doped silicon *Journal of Applied Physics* **89**, 4289–4293.
- [85] D. Yang, R. Fan, L. Li, and D. Que, (1996) Effect of nitrogen-oxygen complex on electrical properties of Czochralski silicon, *Applied Physics Letters* **68**, 487–489.
- [86] J. D. Murphy, C. R. Alpass, A. Giannattasio, S. Senkader, R. J. Falster, and P. R. Wilshaw (2006) Nitrogen in silicon: Transport and mechanical properties *Nuclear Instruments and Methods in Physics Research B* **253**, 113–117.
- [87] D. S. Li, D. R. Yang, E. Leoni, S. Binetti, and S. Pizzini (2004) Photoluminescence of dislocations in nitrogen doped Czochralski silicon. *Chinese Physics Letters* **21**, 2242–2244.
- [88] I. Yonenaga (2005) Nitrogen effects on generation and velocity of dislocations in Czochralski-grown silicon *Journal of Applied Physics* **98**, 023517.
- [89] G. Wang, D. Yang, D. Li, Q. Shui, J. Yang, and D. Que, (2001) Mechanical strength of nitrogen-doped silicon single crystal investigated by three-point bending method, *Physica B*, **308–310**, 450–453.
- [90] X. Yu, D. Yang, X. Ma, L. Li, and D. Que, (2003) Hydrogen annealing of grown-in voids in nitrogen-doped Czochralski grown silicon, *Semiconductor Science and Technology* **18**, 399–403.
- [91] X. Yu, D. Yang, X. Ma, J. Yang, L. Li, and D. Que (2002) Grown-in defects in nitrogen-doped Czochralski silicon *Journal of Applied Physics* **92**, 188–197.
- [92] C. Cui, D. Yang., X. Yu, X. Ma, L. Li, and D. Que, (2003) Effect of nitrogen doping on the minority carrier lifetime in Czochralski silicon, *Microelectronic Engineering* **66**, 373–378.
- [93] T. Fukuda and A. Ohsawa, (1992) Mechanical strength of silicon-crystals with oxygen and or germanium impurities, *Applied Physics Letters* **60**, 1184–1186.
- [94] H. Li, D. Yang, X. Yu, X. Ma, D. Tian, L. Li, and D. Que, (2004) The effect of germanium doping on oxygen donors in Czochralski-grown silicon, *Journal of Physics: Condensed Matter* **16**, 5745–5750.
- [95] X. Yu, D. Yang, X. Ma, H. Li, Y. Shen, D. Tian, L. Li, and D. Que, (2003) Intrinsic gettering in Germanium-doped Czochralski Silicon Crystals, *Journal of Crystal Growth* **250**, 359.
- [96] D. Yang, X. Yu, X. Ma, J. Xu, L. Li, and D. Que, (2002) Germanium effect on void defects in Czochralski silicon, *Journal of Crystal Growth* **243**, 371–374.
- [97] R. H Hopkins R. G. Seidensticker, J. R. Davis, P. Rai-Choudhury, P. D. Blais, and J. R. McCormicket, (1977) Crystal growth considerations in the use of “solar grade” silicon, *Journal of Crystal Growth*, **42**, 493–498.
- [98] *Workshop on Silicon for a growing PV industry, The need to establish a reliable supply of solar grade silicon*, July 2002.
- [99] Information on the workshop program available upon request at solar@ecn.nl
- [100] G. Coletti, (2009) Silicon feedstock: Silicon feedstock: options and specifications, *CrystalClear Final Event*, Sofitel Munich Bayerpost, Munich, Germany, 26 May 2009. Information on the workshop program available upon request at solar@ecn.nl.
- [101] See Section 3.4 and reference therein.

- [102] S. Riepe, I. E. Reis, W. Kwapil, M. A. Falkenberg, J. Schön, H. Behnken, J. Bauer, D. Krefßner-Kiel, W. Seifert, and W. Koch, (2011) Research on efficiency limiting defects and defect engineering in silicon solar cells – results of the German research cluster SolarFocus, *Physica Status Solidi C*, **8**, 733.
- [103] Semiconductor Equipment and Materials International (SEMI), (2003) <http://www.semi.org>, *SEMI M16-1103 Specification for polycrystalline silicon* and recent revisions.
- [104] Japan Electronics and Information Technology Industries Association (JEITA), <http://www.jeita.or.jp>, *JEITA EM3601A Standard specification for high purity polycrystalline silicon*.
- [105] B. Ceccaroli and O. Lohne, (2003) Solar grade silicon feedstock, in *Handbook of Photovoltaic Science and Engineering*, A Luque and S. Hegedus, (eds) Wiley, West Sussex, England.
- [106] J. Nyhus, (2010) Solar grade silicon – history, chemistry and standardization, *Silicon for the Chemical and Solar Industry X*, Norway, June 28 – July 2, 2010 pp. 179–190, Ålesund, Geiranger, Norway.
- [107] SEMI (Semiconductor Equipment and Materials International). <http://www.semi.org/node/38261>.
- [108] *SEMI PV17-0611*, (2011) Specification for Virgin Silicon Feedstock Materials for Photovoltaic Applications.
- [109] General Administration of Quality Supervision, Inspection and Quarantine of the PRC (AQSIQ)
- [110] R. S. Hockett, (2008) Analytical techniques for P V Si feedstock evaluation, *Proceedings of the 18th Workshop on Crystalline Silicon Solar Cells & Modules, Materials and Processes*, August 3–6, 2008, Vail, Colorado, edited by B. L. Sopori, pp. 48–59.
- [111] C. C. Swanson, A. J. Filo, and J. P. Lavine, (2001) Measurement of ultra-trace level metallic impurities in silicon wafers utilizing neutron activation analysis, *Journal of Radioanalytical and Nuclear Chemistry*, **248**, 69–74.