



**Impurities in silicon
and their impact on solar cell performance**

Gianluca Coletti

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In the cover: "Silicon can power the world" (silicon chunk image courtesy of SolarWorld A.G.)

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**Impurities in silicon
and their impact on solar cell performance**

**Onzuiverheden in silicium
en hun invloed op de prestaties van zonnecellen**
(met een samenvatting in het Nederlands)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR AAN DE UNIVERSITEIT UTRECHT
OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. G.J. VAN DER ZWAAN
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- G. Coletti, D. Macdonald, D. Yang, *Role of impurities in solar silicon* in *Advanced silicon materials for photovoltaic applications*, Edited by S. Pizzini, Wiley, in publication. (Chapter 1, 2, 3 and 5)
- G. Coletti, L.J. Geerligs, P. Manshanden, C. Swanson, S. Riepe, W. Warta, J. Arumughan, R. Kopecek, *Impact of iron and molybdenum in mono and multicrystalline float-zone silicon solar cells*, *Solid State Phenomena*, vols 131-133, 15, (2008). (Chapter 4.1)
- G. Coletti, P.C.P. Bronsveld, G. Hahn, W. Warta, D. Macdonald, B. Ceccaroli, K. Wambach, N. Le Quang, J.M. Fernandez, *Impact of metal contamination in silicon solar cells*, *Advanced Functional Materials*, 21, 879 (2011). (Chapter 4.2)
- G. Coletti, R. Kvande, V.D. Mihailetchi, L.J. Geerligs, L. Arnberg, E.J. Ovrelid, *Effect of iron in silicon feedstock on p- and n-type multicrystalline silicon solar cells*, *Journal of Applied Physics*, 104, 104913 (2008). (Chapter 4.3)

Introduction

Direct conversion of solar energy into electricity is a rapidly growing technology. More than 80% of global solar cell production is currently based on silicon^[1]. In the past three decades silicon PhotoVoltaic (PV) modules have experienced an average price reduction of 20% for every doubling of the accumulated sales. The availability of silicon of (assumed) sufficient chemical purity ($>7\text{ N}$), however, has been an important limiting factor for rapid growth and price reduction during part of the past decade and may become one again in the future. The very high cost of investment for conventional poly-Si production plants is a barrier to solve this bottleneck, and becomes even more problematic in times of financial crisis. Furthermore, alternative production processes with lower energy consumption and hence, shorter energy-payback times and smaller carbon footprints based on the corresponding silicon become more important as overall sustainability of energy technologies is set as a development target. Therefore, there is a strong need for low-cost and low investment-cost technologies for the production of silicon for PV applications. However, such low-cost production technologies will most likely compromise the purity of the resultant silicon. For example, construction materials (like steel or graphite used in new types of reactors) or reactants (such as Zn to reduce chlorosilane, C and Al) may influence the quality of the silicon. Also, some low-cost production technologies rely on not purifying the raw (metallurgical) silicon to the same extent as the conventional technologies. Therefore it is crucial to have accurate specifications for concentrations of impurities that could be allowed in silicon feedstock for PV applications (commonly described as 'solar grade silicon') without risking the ambitious yield and cost targets on system level, and achieving shorter energy pay-back times at the same time.

The groundbreaking research performed in the 1970's and 1980's by Westinghouse Corp^[2] (WH study) is still used as a reference for the effect of impurities on solar cell performance. However, because of numerous improvements in cell processes since then, and the increased use of directionally solidified multicrystalline ingots^[3] instead of single-crystalline ingots, there is a need for updated and more detailed studies.

Impurities in crystalline silicon can be classified in two categories, dopants and contaminants. Generally, dopants are intentionally added to modulate the resistivity, while contaminants are unintentionally incorporated during various phases of material manufacturing and subsequent processing. However, also *removal* of dopants like P and B present in too high concentrations in source materials is a crucial step in silicon purification. Unfortunately, especially new, low-cost processes are less effective in this respect. This is mainly due to the large segregation

coefficients of dopants, which limits the possibilities of their removal by zone refining.

The quality of silicon depends on the purification processes associated with the manufacturing of the polysilicon feedstock starting from metallurgical silicon. However, during the entire manufacturing chain which leads to solar cells (and modules), both purification and contamination processes take place.

The aim of the studies presented in this thesis is to understand the complex relation between the impurity content of the silicon starting material (the “feedstock”) and the resulting solar cell device performance, taking into account the effects of processing and device architecture. In Chapter 1 of this thesis the different sources of impurities and the related refinement processes are discussed. The impurity segregation mechanism during the crystallisation of silicon ingots is reported in Chapter 2. In Chapter 3 the role of metal impurities in crystalline silicon is described. The impact of metal impurities on the solar cell performance is discussed separately in chapter 4. This is divided into 4 sections. In the first section (Section 4.1) the impact of Fe and Mo in Float Zone (FZ) silicon rods is reported. Section 4.2 discusses the impact of Fe in both p- and n-type multicrystalline silicon (mc-Si) ingots while Section 4.3 reports the role of Fe, Ni, Cr, Ti and Cu in p-type mc-Si. The specifications for solar silicon are discussed in Chapter 5.

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Impurities in silicon: sources and mitigation of their effect on solar cell performance

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. 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 this chapter we consider where these impurities come from and how they are/could be removed or passivated.

Figure 1.1¹ illustrates the main sources of impurities along the overall production chain of crystalline silicon PV modules. 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, aluminium, titanium, calcium and cobalt. Dopant elements for silicon like boron and phosphorous 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, phosphorous, sulphur, 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.

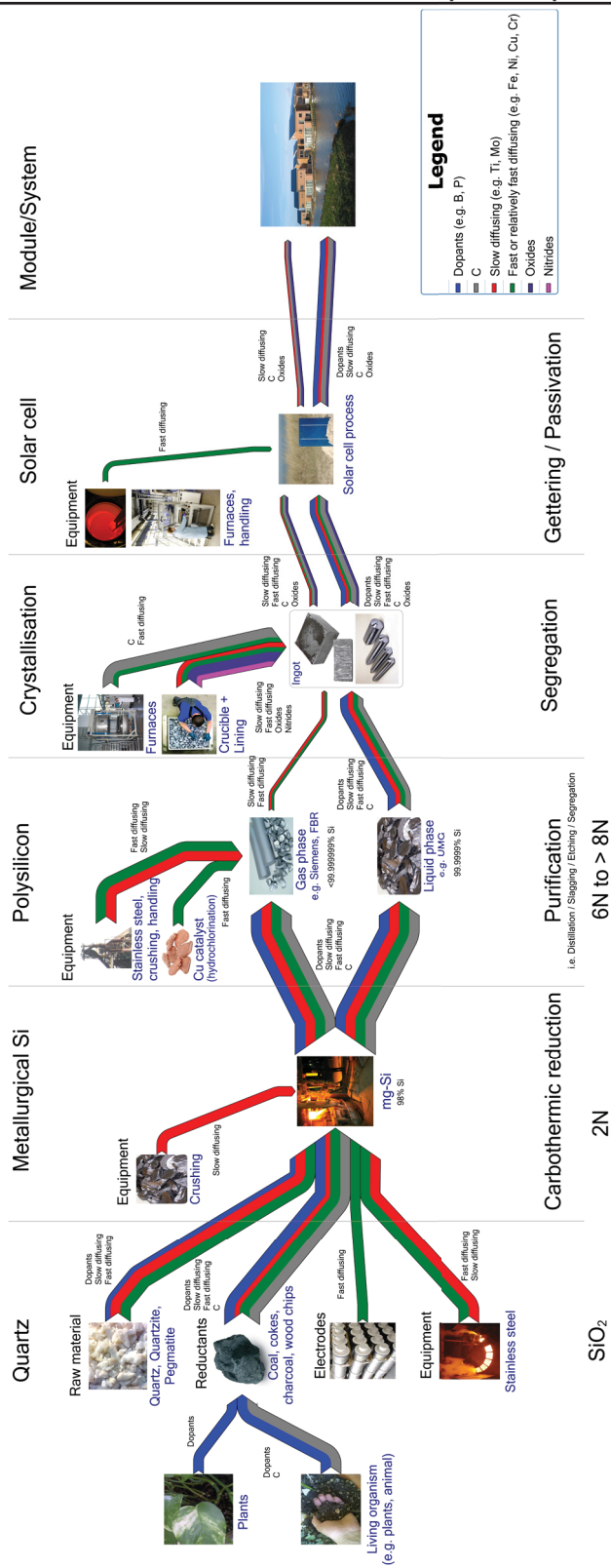


Figure 1.1 Impurity sources and refinement scheme.

After the carbothermic reduction, silicon 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 mould 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 categorise 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 [2,3].

Gas phase purification consists of a distillation process to obtain silane and chlorosilane. The gases are then decomposed in a rod deposition reactor by a Chemical Vapour Deposition process. This step is also known as the Siemens process. An alternative process has been developed to create polycrystalline granules and powders in a Fluidized Bed Reactor (FBR), with reduced cost and environmental impact. 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, occur, as 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 CVD processes due to contamination from stainless steel parts of the reactors (Siemens process). Contamination from Cu might come from its use as a catalyst to increase the yield of the hydro-chlorination reaction, for example in FBR process. 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^[4].

Liquid phase purification uses metallurgical processes, such as slagging, filtering, leaching, etching with a final stage consisting in a liquid/solid segregation 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 Chapter 2), like most of the transition metals. Silicon dopant

elements like boron and phosphorous are difficult to remove, using a sole liquid/solid segregation process, due to their segregation coefficients close to unity. Aluminium is also difficult to be removed due to its relatively large segregation coefficient. Its presence, or that of Zn, is systematic in feedstocks which use Al or Zn as reducing agents for the purification. Carbon contamination is a direct consequence of the carbothermic reduction of quartz but arises as well 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 which 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 Chapter 4 the effects of transition metals and their mitigation are discussed. The effect of dopants and light elements on solar cell performance and their mitigation are extensively discussed in literature ^[5].

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 1.1. Each technique has different ways to melt the silicon, seed the crystallisation and pull or cast the ingots, consequently, the associated contamination is different, as it is shown in Table 1.1 where the different sources of contamination are listed.

Table 1.1 Crystallisation 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, Mould Substrate Hot-zone parts	C, transition metals

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 which 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 the silicon with the crucible. This is observed in multicrystalline ingots as well due to inefficiencies in the coating with Si_3N_4 . The oxygen is dissolved in the silicon melt as SiO and forms by a partial reduction of silica with silicon. Being very volatile, it sublimates from the liquid/gas phase^[6] interface, 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 progression and so does the volume/surface ratio. Therefore the concentration of SiO in the Si melt decreases and, as a consequence, the content of oxygen in the solid silicon decreases as well. The final oxygen profile in the ingot depends, however, not only on the occurring of this process, but also on the simultaneous process of oxygen segregation between the liquid and solid silicon phase. 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 crystallisation 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 crystallisation completion and during the cooling down, 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^[7].

In addition, during the crystallisation, the bottom and side parts of multicrystalline ingots are still at high temperature and are in direct contact with the crucible^[8] and with the lining. Therefore impurities present in the lining, mainly the fast or relatively fast diffusers like Fe, can diffuse into the solid silicon^[9].

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 1.2.

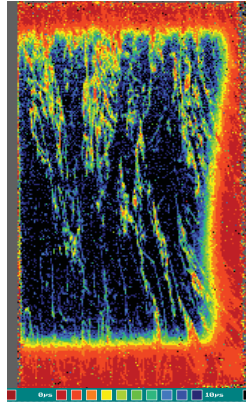


Figure 1.2 Lifetime map of a cross section of a multicrystalline ingot (courtesy of Photowatt Technologies).

The side edges of any ingot show this impurity diffusion effect. The side "red zone" is broader 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 which 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 (e.g. 156 x 156 mm²). 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 which 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 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 de-ionised water employed, in order to avoid re-plating 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 SiN_x:H deposition and contact formation. Impurity gettering^[10,11] is a kind of solid/solid segregation process, caused by the higher solubility of impurities in the

phosphorous (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^[12, 13] the electronic properties of the silicon substrate increase 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 involved^[14]. 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. Cross contamination 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^[15,16,17,18] 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^[19].

High temperature processes can cause precipitation of light elements such as C and O, as SiC or SiO₂, which is often accompanied by the formation of extended defects and/or interaction with other impurities.

The hydrogenation^[20] 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 impurity source is not only the quartz employed but 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 and are integral part of the silicon refinement process.

In particular, segregation during crystallisation 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^[21], 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 status (for example by precipitation) during high temperature processes, with various effects on the lifetime and on the solar cell performance.

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Segregation of impurities during silicon growth

Crystallisation 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 discovered by Fischler ^[1,2] already in the 1960's. Since the solid solubility of impurities in silicon 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.

2.1. Equilibrium segregation coefficient

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. The 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,

$$k_{eq} = \frac{C_s}{C_L} \quad (2.1)$$

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 atom sizes. Figure 2.1 shows the correlation of the equilibrium impurity segregation coefficients in silicon as a function of their atom sizes.

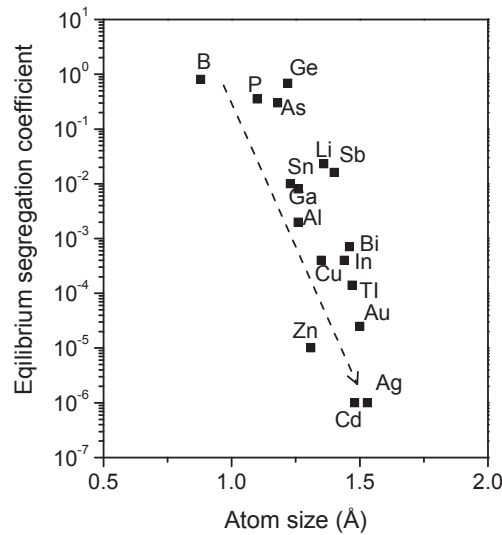


Figure 2.1 Equilibrium segregation coefficients in silicon versus the radius of impurity atoms. After D. Yang, in G. Coletti, D. Macdonald, D. Yang: *Role of impurities in solar silicon; in Advanced silicon materials for photovoltaic applications*. Edited by S. Pizzini, Wiley, in publication.

2.2. 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 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 behaviour of impurities during silicon crystal growth. This effect was analysed by Burton, Prim and Slichter^[3] 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 Fig 2.2.

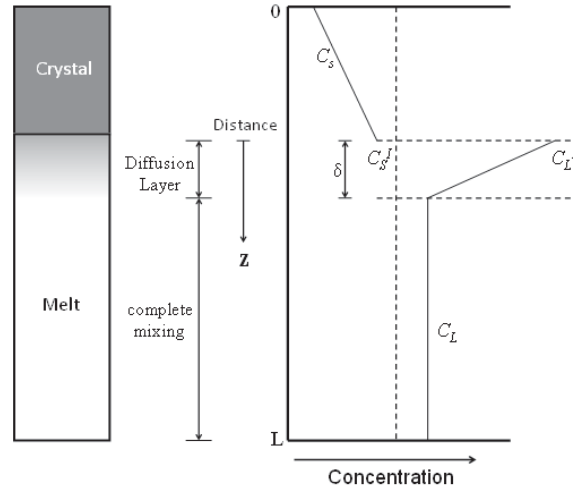


Figure 2.2 Schematic diagram of one-dimensional crystal growth, containing a boundary layer with thickness δ , and a region of complete mixing. After D. Yang, in G. Coletti, D. Macdonald, D. Yang: Role of impurities in solar silicon; in *Advanced silicon materials for photovoltaic applications*. Edited by S. Pizzini, Wiley, in publication.

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

$$C(z) = B + (C_L^I - C_S^I) \exp\left(-\frac{\nu z}{D}\right) \quad (2.2)$$

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 concentrations at the interfaces.

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

$$C_L = B + (C_L^I - C_S^I) \exp\left(-\frac{\nu \delta}{D}\right) \quad (2.3)$$

Using equations (2.2) and (2.3), we can obtain

$$0 \leq z \leq \delta, \quad C(z) = C_L + (C_L^I - C_S^I) \left(\exp\left(-\frac{\nu z}{D}\right) - \exp\left(-\frac{\nu \delta}{D}\right) \right) \quad (2.4-a)$$

$$\delta \leq z \leq L, \quad C(z) = C_L; \quad (2.4-b)$$

At the crystal/melt interface,

$$C_L^I = C_L + (C_L^I - C_S^I) \left(1 - \exp \left(-\frac{v\delta}{D} \right) \right) \quad (2.5)$$

Equation (2.5) can be changed into

$$1 = \frac{C_L}{C_S^I} - \left(\frac{C_L^I}{C_S^I} - 1 \right) \exp \left(-\frac{v\delta}{D} \right) \quad (2.6)$$

Note that if the effective segregation coefficient is defined as $k_{eff} = \frac{C_S^I}{C_L}$ and the equilibrium segregation coefficient is $k_{eq} = \frac{C_S^I}{C_L^I}$ then equation (2.6) can be written as

$$k_{eff} = \frac{1}{1 + \left(\frac{1}{k_{eq}} - 1 \right) \exp \left(-\frac{v\delta}{D} \right)} \quad (2.7)$$

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 (2.7) reduces to $k_{eff} \cong k_{eq}$ and for $v\delta/D \gg 1$, i.e. fast solidification and/or no mixing ($\delta \rightarrow \infty$), equation (2.7) reduces to $k_{eff} \cong 1$, implying full incorporation. From equation (2.7), it can also be noted that with an increase of crystal growth rate, the value of k_{eff} increases.

Table 2.1 shows the effective segregation coefficients k_{eff} of various impurities in silicon.

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 represent equilibrium segregation coefficients.

Table 2.1 Measured segregation coefficients of main impurities in silicon

Segregation coefficients					
Method		FZ		Cz	mc-Si
		k_{el}	k_{eff}	k_{eff}	k_{eff}
Technique	Reference	DLTS	NAA	NAA	NAA
Growth speed		Lemke ^[4]	Coletti ^[5]	Davis ^[6]	Coletti ^[7]
		20 cm/h	~9 cm/h	7 cm/h	~1.5 cm/h
Element					
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}	

The comprehensive work on segregation coefficients carried out by Lemke ^[4] 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. ^[5] 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. ^[6] 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 ^[5] and in Cz ^[6], 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 [5] and [6] 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 Chapter 3 on the role of transition metals). Coletti et al. ^[7] (Table 2.1) 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 ^[8] on mc-Si. Both the data in [8] and [7] 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 [8], 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 which has a segregation coefficient ^[9] close or equal to 1 (see Chapter 1 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 ^[10], instead of 0.33 as was generally accepted.

2.3. Distribution of impurity in silicon crystal due to segregation

During the crystallisation an overall solute balance between the liquid silicon and the solid is established. This balance is expressed in a differential equation which takes into account the characteristics of different crystallisation techniques. In case of Cz and directional solidification growths, the liquid volume decreases with the

crystallisation progress. The total amount of impurities in the crystal and in the melt should remain constant, and can be written as,

$$\int_0^f C_S dx + (1-f)C_L = C_0 \quad (2.8)$$

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

$$C_S + (1-f)\frac{dC_L}{df} - C_L = 0 \quad (2.9)$$

Considering $C_S = k_{eff} C_L$, equation (2.9) becomes

$$\frac{dC_L}{C_L} = \frac{(1-k_{eff})}{(1-f)} df \quad (2.10)$$

By applying the boundary condition that $C_L = C_0$ at $f = 0$, equation (2.10) can be solved as ,

$$C_S = k_{eff} C_0 (1-f)^{k_{eff}-1} \quad (2.11)$$

This expression is the so called “normal freezing equation” ^[11] describing the distribution of impurity concentrations along the axial direction.

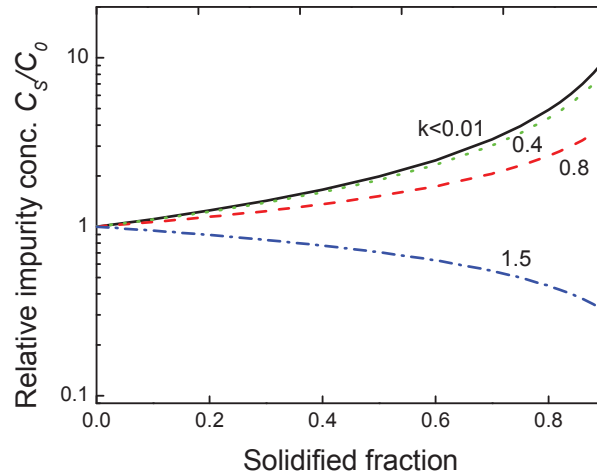


Figure 2.3 Relative distribution of impurities with different k values along the axial direction of a silicon ingot.

Figure 2.3 shows the distribution of impurities along the axial direction of a silicon crystal for different values of k_{eff} . For $k_{eff} < 1$, 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 non-physical conditions since there are solubility limits (second phase formation) to how high the solid and liquid concentrations can increase due to segregation. For $k_{eff} > 1$, the solidified crystal part contains more impurities, 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.

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Role of metal impurities in crystalline silicon

In this Chapter we discuss the effect of metallic impurities on the material 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 status and distribution depends mainly on the solubility and the diffusivity which 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 band gap, which increase recombination of charge carriers, and therefore strongly affect the electronic material properties.

3.1. Solubility and diffusivity

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

$$S = S_0 e^{-\frac{H_s}{kT}} \quad \text{for } T < T_{\text{eut}} \quad (3.1)$$

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 metal becomes increasingly supersaturated. To avoid superaturation, 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

$$D = D_0 e^{-\frac{H_M}{kT}} \quad (3.2)$$

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 an area 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. Gettering effects are extensively detailed in literature ^[1].

Since each dissolved impurity can act as a recombination centre, 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. This is true if the minority carrier capture radius of these precipitates is sufficiently smaller than the distance between them. In general the capture cross section of a precipitate is, among other things, a function of its size ^[2,3,4] 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 ^[5].

Fig. 3.1 shows the solubility of the main impurities in silicon as a function of the diffusivity ^[6,7]. 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 Fig. 3.1. For a target value of impurity concentration (equilibrium solubility) the graph shows the corresponding diffusivity. At 840 °C, which is the typical temperature for phosphorous diffusion, the solubility of Ti is extremely low, however 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 very difficult to treat, being insensitive to any gettering process. Fast or relatively fast impurities like Cu and Fe are not as harmful even at relative 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 ^[8,9].

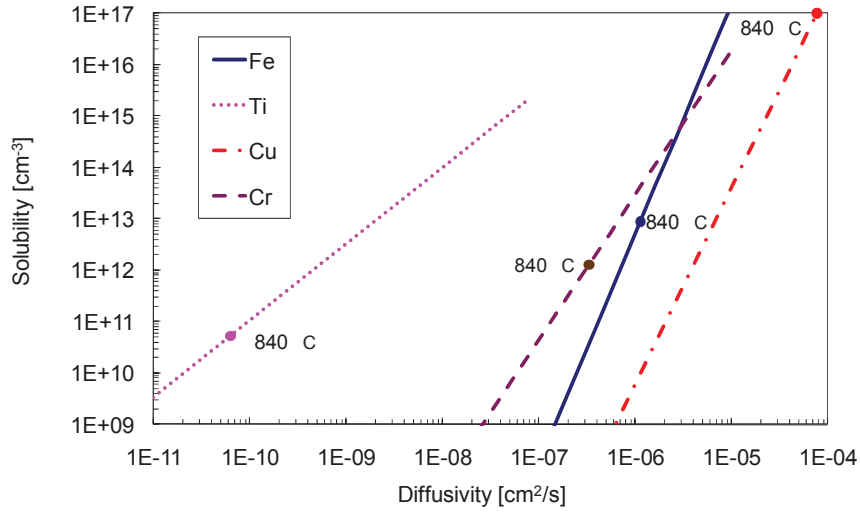


Figure 3.1 Solubility versus diffusivity for representative metals. The dots represent the solubility and diffusivity at 840 °C, which is the typical temperature for P-diffusion.

3.2. 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 reduce the conversion efficiency. Deep levels in the silicon band gap, caused by defects and impurities, increase this recombination. Such defect-assisted recombination is referred to as Shockley Read Hall (SRH) ^[10,11] recombination. The minority carrier lifetime from the SRH theory can be written as:

$$\tau_{\text{SRH}} = \frac{\tau_{n0}(p_0 + p_1 + \Delta n) + \tau_{p0}(n_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} \quad (3.3)$$

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 u_{th} and the defect concentration N_t via $\tau_{n0}^{-1} = N_t u_{\text{th}} \sigma_n$ and $\tau_{p0}^{-1} = N_t u_{\text{th}} \sigma_p$. 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 $\Delta n = \Delta p$.

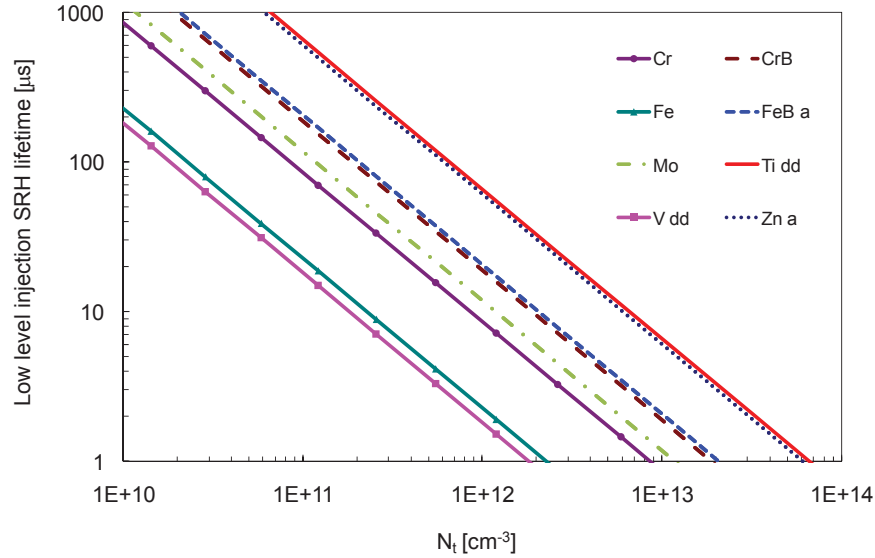


Figure 3.2 SRH lifetime of several impurities in Si as a function of defect concentration at low injection level for a bulk resistivity of 1 Ωcm . In the legend a) means acceptor and dd) double donor.

The importance of this expression is that it allows modelling 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 Fig 3.2 the lifetime predicted by the SRH theory for several impurities is plotted as a function of the defect concentration. The lifetime is calculated at low injection level ($\Delta n \ll p_0$, n_0 , $\Delta n \ll n_1$) for p-type silicon with a bulk resistivity of 1 Ωcm . The lifetime at low level injection is a reasonable approximation for typical solar cell operation conditions, especially in case 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 Eq. 3.3 reduces to:

$$\tau_{SRH} = \tau_{n0} \left(1 + \frac{1}{p_0} \left(p_1 + \frac{\tau_{p0}}{\tau_{n0}} n_1 \right) \right) \quad (3.4)$$

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 Fig. 3.3 the lifetime versus injection level of 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 (Fig 3.3 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

injection level, the lifetime increases considerably. Since at low defect concentrations (Fig. 3.3 p-type top graph) the injection level corresponding e.g. at 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.

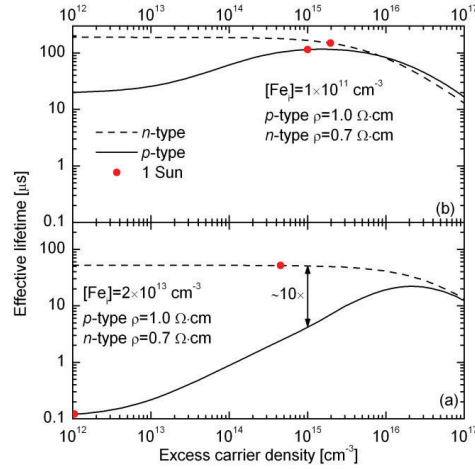


Figure 3.3 SRH lifetime of interstitial Fe as function of the injection level. The lifetime corresponding to an illumination of 1 Sun is shown for two different Fe concentrations assuming no other defect in the bulk are present. The difference in p- and n-type is also shown. An emitter recombination current (J_{0e}) of $1 \times 10^{-13} \text{ A/cm}^2$ has been used. Band-to-band and Auger recombination were considered.^[12]

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 Fig. 3.2.

Besides this, in Fig. 3.2 it is visible that the Ti double donor, a state which 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.

3.3. Interaction of impurities with the crystal structure

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 observed (see Chapter 4). Indeed a poorer crystallographic structure has been reported ^[12,13] in ingots with high concentrations of iron, chromium, nickel and copper in comparison to reference uncontaminated ingots. Smaller grains and highly dislocated areas are found in the bottom and top of the ingots and do not seem to be related to the specific species added but rather on 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 ^[8,9] and therefore the impurity impact on the cell performance is heightened. Section 4.3 shows the increase in extended defect density in an ingot contaminated with iron in comparison to reference uncontaminated ingots.

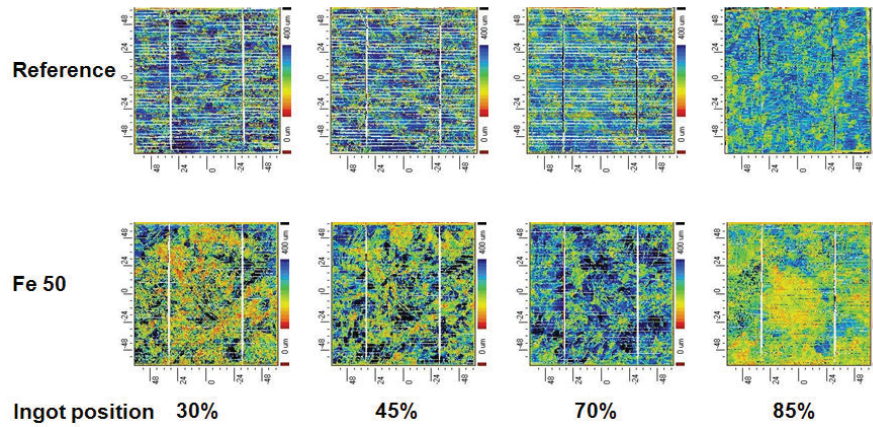


Figure 3.4 Diffusion length map of solar cells from a p-type ingot contaminated with 50 ppm wt of iron and reference as a function of the ingot position.

Another type of interaction between impurities and crystallographic defects has been shown by Pizzini et al. in [14] who reported a sensible increase in the recombination activity of grain boundaries (GBs) in presence of high concentration of V, Ti or Cr. However a redistribution of O between grain volume and GBs has been observed as a result of a heat treatment, because of which an influence of impurity-oxygen interaction on the phenomena cannot be excluded. In case of Fe ^[15,14] and Mo ^[15] no clear increase in the recombination activity of crystallographic defects (GBs and dislocations) has been observed between intentionally contaminated and reference wafers.

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 (beside to the impurity recombination parameters) and the precipitates size and distribution as well. This is quite ambitious and a dedicated experimental analysis which relates the initial impurity in the feedstock to the final solar cell efficiency is instead reported in the following sections.

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Impact of metal impurities on the solar cell performance

In this Chapter we discuss the effect of metallic impurities on both the material and device properties. Impurities cause defect energy levels within the silicon band gap, which increase recombination of charge carriers, and therefore strongly affect the material properties. In addition, 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.

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 chapter.

To model the effect of impurities one should know their recombination parameters and concentration in the device, as described in the previous Chapter. 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 modelling 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 situation when one has to predict behaviour, 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 ^[1,2]. However the difficulties are again in knowing the fundamental parameters which determine the physics. Additionally, experimental approaches require a lot of efforts and are time consuming. Characterisation of defects and parameter extractions often require microscopic analysis ^[3,4] and extensive sample preparation which are not easily accessible.

The paramount work carried out in the '70s and '80s 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 Czochralski (Cz) ingots, examined a very wide range of impurities. The main outcome of this work is a model which 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 characterisation facilities, there was a need for updated and more detailed studies^[5].

Recently the author revisited the Westinghouse work, carrying out a systematic study on intentionally contaminated polysilicon and its effect on the solar cell performance^[6,7,8] within the European Integrated project CrystalClear^[9] and the European project Foxy^[10]. Among the most important differences are the facts that the data refers 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 and Float Zone (FZ) ingots, as opposed to Cz silicon ingots. In this updated work the direct relationship between impurities in the feedstock and the final solar cell performance is reported and analyzed. This provides the most straightforward and meaningful interpretation, especially in relation to specifying the feedstock impurity tolerances. The conclusions, therefore, do not rely on impurity analysis or estimated segregation coefficients.

In the following sections the results from these investigations are reported. In Section 4.1 the impact of Fe and Mo in FZ silicon rods is discussed. Section 4.2 reports the impact of Fe in both p- and n-type multicrystalline silicon (mc-Si) ingots while Section 4.3 discusses the role of Fe, Ni, Cr, Ti and Cu in p-type mc-Si.

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4.1

Impact of iron and molybdenum in mono and multicrystalline float-zone silicon solar cells

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Abstract. This paper investigates the impact of iron (Fe) and molybdenum (Mo) when they are introduced in the feedstock for mono- and multicrystalline Float-Zone (FZ) silicon (Si) growth. Neutron Activation Analysis shows that the segregation coefficient is in agreement with literature values. Lifetime maps on monocrystalline wafers show a uniform lifetime which decreases with the increase of contamination levels. Multicrystalline wafers show low lifetime areas, corresponding to grain boundaries and highly dislocated areas, which are independent from the contamination levels. Intra grain areas have a higher lifetime which changes with the contamination levels. The solar cells show a reduced diffusion length in multicrystalline uncontaminated cells compare to the monocrystalline uncontaminated. In multicrystalline cells the lowest level of Fe introduced (10^{12} at/cm³) has hardly any influence, whereas in the Mo-contaminated cells the impact is visible from the lowest level (10^{11} at/cm³). In monocrystalline cells the diffusion length is reduced already at the lowest contamination level of Fe.

1. Introduction

The aim of this work is to provide an updated reference for the role of particular impurities in the current cell process technology for multicrystalline and monocrystalline silicon wafers.

In this work we study the role of iron and molybdenum when intentionally introduced in a silicon melt before the crystallisation of FZ ingots. The reason for the choice for these impurities, as first elements in our overall work, is given in the next section. The impact of the contaminants during industrial solar cells processing will be shown and analysed.

The research performed in the 1980's by Westinghouse Corp ^[1] is still used as reference for the effect of impurities on solar cell performance. However, those results were obtained with cell processing technology of the 1980's, and mostly on monocrystalline material. Our paper shows additional and essential information from the comparison between multicrystalline and monocrystalline Si wafers. Our paper also shows differences in sensitivity of the monocrystalline wafers to impurities, compared to the Westinghouse studies.

2. Approach

The best way to investigate the impact of specific metal contaminants is to intentionally contaminate the material with a well-defined impurity concentration. At the same time the concentrations of other impurities should be kept as low as possible.

Clean material can be most conveniently obtained by producing FZ ingots. FZ ingots can be grown from a mono- or multicrystalline seed, resulting in a mono- or multicrystalline ingot. This permits to study the incorporation and impact of impurities when present together with grain boundaries. It has to be taken into account that the crystal structure and the temperature history are not necessarily comparable to industrial Directionally Solidified (DS) multicrystalline silicon (mc-Si). Unintentional contamination is most unlikely in the FZ growth technique, in contrast to small scale directional solidification. This is a big advantage, which was decisive in our choice for the method.

Choice of the impurities.

The impurities investigated in this work are iron and molybdenum. Fe is a dominant metal impurity in silicon wafers ^[2,5]. It is a relatively fast diffusing impurity ($D = 2.6 \times 10^{-6} \text{ cm}^2/\text{s}$ @ 1000 °C), thus it can be gettered. Mo is not present in similar levels as Fe in silicon wafers but it is very detrimental for the lifetime. It has been detected in cast mc-Si by neutron activation analysis ^[2]. The diffusivity of Mo was investigated by Hamaguchi ^[3] who found a very small value ($D = 2 \times 10^{-10} \text{ cm}^2/\text{s}$ @ 1000 °C) comparable, for example, to Ti. Therefore precipitation and gettering are expected to be significantly different from Fe, and it can be considered as a model impurity for other slow diffusing impurities.

Material

Fourteen boron-doped ingots (target resistivity 1 $\Omega \cdot \text{cm}$) were grown with pedestal growth technique ^[4] (see Fig. 1) at Institut für Kristallzucht (IKZ) Berlin. Three levels of impurities of each element were introduced in both mono- and multi-crystalline ingots (see Tab. 1). The target levels in the solid were chosen taking into consideration both typical level in silicon wafer (see [1] and [5]) and minimum level in order to see an effect on the minority carrier recombination ^[6]. Two reference ingots (mono- and multicrystalline) were grown without added impurities.

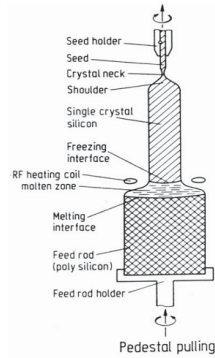


Figure 1 Schematic depiction of pedestal FZ-Si ingot growth technique^[4].

Table 1 Impurity concentration introduced in the silicon melt during the growing process.

Impurity Cont. level	Mo	Fe
	ppma	
1	25 mc-	2.6 mono mc-
2	240 mc-	54 mono mc-
3	2800 mono mc-	860 mono mc-
Westinghouse	8-1900 c-Si ~1000 mc-	53-5300 c-Si 1900 mc-, partly analysed

In the last row the impurity concentration analysed in the Westinghouse study^[1] is reported for comparison.

The very low segregation coefficient of Fe and especially Mo together with the high base doping result in a high concentration of impurities in the silicon melt, which causes dislocations in the crystal lattice. The presence of dislocations in the crystals causes residual stress at room temperature which can cause ingot breakage especially during wafering. The maximum ingot diameter to avoid breakage during the cool down phase is 40 mm. In order to release the remaining residual stress the ingots were annealed at 1000 °C for 3 h with a slow cool down. The contamination due to annealing furnace was tested and its impact is considered negligible.

To study the change in the electrical activity of the material after annealing, due to e.g. the formation or the dissolution of precipitates, part of the ingots were cut into wafers and characterised before annealing despite the residual stress. The Quasi Steady State - PhotoConductance (QSS-PC) lifetime measurements reveal hardly a significant change in the electrical activity due to the thermal treatment. Only one monocrystalline Mo-doped ingot could, so far, be processed because the other ingots were too fragile before annealing.

In the remainder of this paper, all the characterisation and solar cell process results are obtained on material after annealing if not differently specified. The wafer and solar cell characterisation before annealing was reported in [7].

3. Results and discussion

Neutron Activation Analysis

Neutron Activation Analysis (NAA) is a technique successfully applied to silicon for the detection of impurity elements at very low concentration levels^[8]. NAA provides the total number of the elements present, regardless of their electrical activity. The concentration level reported assumes a homogenous distribution of the impurity in the sample. This assumption is largely confirmed as revealed by the lifetime map of spatial homogeneity (see next section).

Wafers with a thickness of about 3 mm were cut from each ingot for NAA. After a chemical etch the samples were irradiated at the Washington State University with a thermal neutron flux of 2.5×10^{12} n/cm²/s for 75 h. The samples were then counted for gamma emission at the Eastman Kodak Company Research Labs in order to

obtain concentration levels of several elements. The lowest Fe and Mo concentrations detected in the silicon matrix were 10^{13} at/cm³ and 5×10^{11} at/cm³ respectively.

In Fig. 2 the levels of iron and molybdenum detected with NAA are reported versus the known amounts of impurity introduced in the melt. The solid concentrations are found to be proportional to the liquid concentrations for both Mo and Fe ingots. Deviation is found for the lowest Fe concentration.

The slope of the straight line through the points is a measurement of the effective segregation coefficient (K_{eff}), thus found for both Mo and Fe, is in agreement with the value of the equilibrium segregation coefficient (K_{eq}) reported in literature [1, 9].

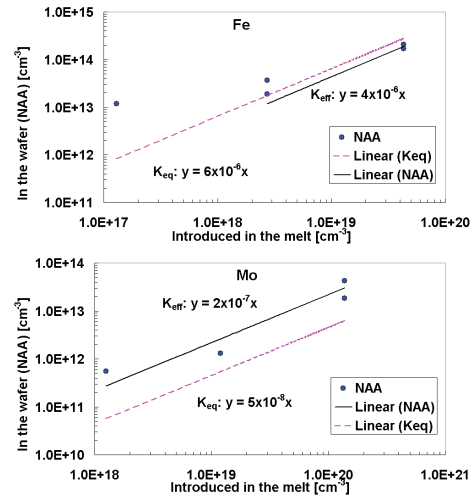


Figure 2. Iron (top) and molybdenum (bottom) concentration in the solid versus their concentration introduced in the Si melt. The solid line is a linear fit of the data points. The dashed lines show the equilibrium segregation coefficients reported in literature [1,9].

Lifetime maps

For surface passivation, the wafers were subject to a chemical polishing and a cleaning followed by a Plasma Enhanced-Chemical Vapour Deposition SiN_x deposition optimised for surface passivation. The effective lifetime measured represents the lifetime in the bulk of the wafers. Modulated Free Carrier Absorption (MFCA) [10] measurements were performed. In Fig. 3 lifetime maps are reported.

Multicrystalline wafers

The multicrystalline wafers show areas with high and low lifetime. The low lifetime areas show a pattern typical for grain boundaries and dislocated areas, similar to what is observed in directionally solidified mc-Si. There appears to be no clear difference in recombination activity of the crystal defects in the different wafers (see Fig. 3), but this has not yet been analysed quantitatively.

The high lifetime areas, which coincide with intra grains areas, have a lifetime which decreases with the increase of Fe and Mo level.

In Fig. 4 the lifetime distribution within each wafer is reported for each contaminant level.

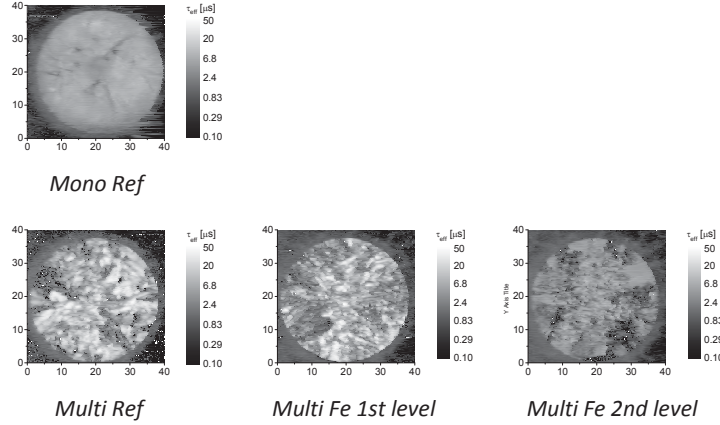


Figure 3. Lifetime map (Modulated Free Carrier Absorption) of as-cut wafers with different level of Fe and uncontaminated.

Monocrystalline wafers

The lifetime map in monocrystalline wafers is uniform apart from a limited inhomogeneity in the centre of some wafers (see Fig. 3 Mono Ref). This inhomogeneity corresponds to the presence of dislocations.

The lifetime decrease with the increase of Fe level.

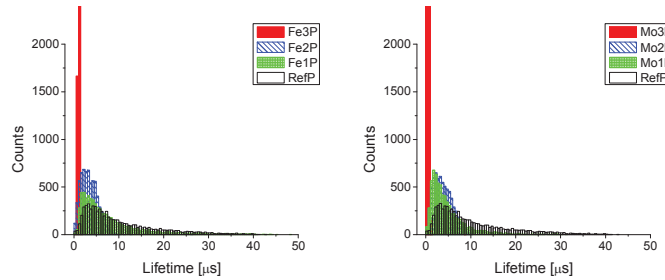


Figure 4. Lifetime distribution of Fe (left) and Mo (right) multicrystalline wafer measured by MFCA.

Solar cell results

The solar cell process was based on a standard industrial firing-through- SiN_x process. In order to apply the same process to mono- and multicrystalline wafers, the wafer surface was polished. The wafers received a phosphorous diffusion in a belt furnace, and a remote plasma-enhanced CVD of SiN_x at ECN. The SiN_x is optimised for multicrystalline Si wafers in order to obtain a good anti-reflective coating as well as bulk- and surface-passivation properties. The screen-printed metallisation and co-firing was carried out at the University of Konstanz. The solar cells were then cut to $2 \times 2 \text{ cm}^2$ by a dicing saw. The solar cell efficiency on reference directionally solidified mc-Si was about 14.5% on polished etched wafers (15% on alkaline etched wafers).

The solar cell process was carried out on two neighbouring wafers for each impurity level.

The Voc of cells on uncontaminated substrates is 625 mV for the mono c-Si substrate and 593 mV for the mc-Si substrate. The latter is quite low. The large amount of crystal defects seems to have a significant impact on the solar cell performance.

Spectral response and reflectance measurements were carried out on all solar cells to determine the Internal Quantum Efficiency (IQE). The IQE curves are reported in Fig. 5. A decrease in the quantum efficiency at long wavelength is observed with increase of contamination level for both elements. The IQE at short wavelength is comparable for all the cells. This shows the stability of the solar cell process. In addition, at even high concentration level, the emitter recombination and surface passivation properties are not influenced by the impurities.

The diffusion length was calculated from the slope of the curve $1/\text{IQE}$ versus $1/\alpha(\lambda)$ [11]. The results are reported in Table 2

Table 2 Effective diffusion length as calculated from the $1/\text{IQE}$ versus $1/\alpha(\lambda)$ curves.

Sample	Ref	Fe-1	Fe-2	Fe-3	Mo-1	Mo-2	Mo-3
L_{Diff} [μm]							
Mono	540	260	110	100	-	-	40
Multi	180	140	90	70	120	75	30

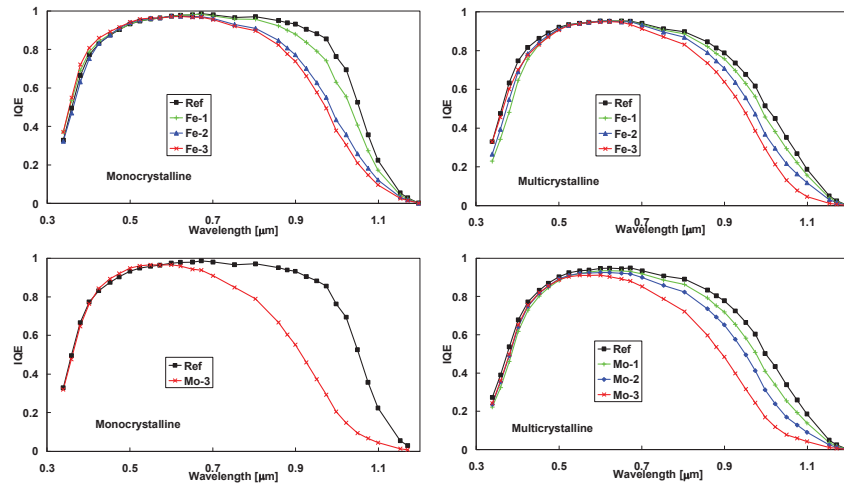


Figure 5. Top left: Fe-contaminated and reference mono-Si. Top right: Fe-contaminated and reference mc-Si. Bottom left: Mo-contaminated and reference mono-Si. Bottom right: Mo-contaminated and reference mc-Si. The quantum efficiency is strongly reduced at long wavelength with the increase of impurity level.

The IQE at long wavelength for the uncontaminated multicrystalline solar cells is much lower than in monocrystalline wafers. The reduction in the diffusion length is more than 60%. The crystal defects should be the only cause for this decrease. The first level of Fe introduced (10^{12} at/cm³) has hardly any influence on mc-Si cell

performance. For Mo, however, an impact is visible at the lowest level (10^{11} at/cm³). In monocrystalline wafers the diffusion length is reduced already at the lowest contamination level of Fe. However this is barely visible on cell performance because the diffusion length is anyway higher than the solar cell thickness.

The change in recombination from wafer to cell and the specifications for the SoG-Si feedstock will be discussed in a forthcoming publication.

4. Conclusions

This paper investigates the impact of Fe and Mo in FZ ingots. NAA shows that the segregation coefficient is in agreement with literature values. Lifetime maps on monocrystalline wafers show a uniform lifetime which decreases with the increase of contamination levels. Multicrystalline wafers show low lifetime areas, corresponding to grain boundaries and high dislocated areas, which are independent from the contamination levels. Intra grain areas have a higher lifetime, which changes with the contamination levels. The solar cells show a reduced diffusion length in multicrystalline uncontaminated cells compare to the monocrystalline uncontaminated. In multicrystalline cells the lowest level of Fe introduced (10^{12} at/cm³) has hardly any influence, whereas in the Mo-contaminated cells the impact is visible from the lowest level (10^{11} at/cm³). In monocrystalline the diffusion length is reduced already at the lowest contamination level of Fe. However this is barely visible on cell performance because the diffusion length is anyway higher than the solar cell thickness.

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4.2

Impact of Fe, Cr, Ni, Ti and Cu in multicrystalline silicon solar cells

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Abstract: The impact on solar cell performance of the transition metals iron, chromium, nickel, titanium and copper is investigated. Each impurity is intentionally added to silicon feedstock used to grow p-type directionally solidified multicrystalline silicon ingots. A state of the art screen-print solar cell process is applied to this material. Impurities like iron, chromium and titanium cause a reduction in the diffusion length. Nickel does not reduce the diffusion length significantly, but strongly affects the emitter recombination reducing the solar cell performance significantly. Copper has the peculiarity to impact both base-bulk recombination as well as emitter recombination.

Two models based on the Scheil distribution of impurities are derived to fit the degradation along the ingot. Solar cell performances are modeled as a function of

base-bulk recombination and emitter-bulk recombination. The model fits the experimental data very well and is also successfully validated. Unexpectedly, the distribution of impurities along the ingot, due to segregation phenomena (Scheil distribution), leaves its finger-print even at the end of the solar cell process.

A measure of impurity impact is defined as the level of impurity which causes a degradation in the cell performance of less than 2% up to 90% of the ingot height. The advantage of this impurity impact metric is that it comprises the different impurities physical characters in one single parameter, easy to compare.

1. Introduction

The groundbreaking research performed in the 1970's and 1980's by Westinghouse Corp^[1] (WH study) is still used as a reference for the effect of impurities on solar cell performance. However, because of numerous improvements in cell processes since then, and the increased use of directionally solidified multicrystalline ingots^[2] instead of single-crystalline ingots, there is a need for updated and more detailed studies.

In this work we study the impact of iron, chromium, nickel, titanium and copper on p-type multicrystalline silicon (mc-Si) ingots, with particular emphasis on the properties of the solar cells and the detrimental effect on solar cell performance.

Iron is a dominant metal impurity in silicon, and being a relatively fast diffusing impurity, is sensitive to gettering. Chromium and nickel, as components of steel together with iron, are widely employed as construction material for equipment, often resulting in significant silicon contamination. Copper is a fast diffusing impurity having a high mobility even at room temperature, therefore contamination and in-diffusion of copper is not unlikely. In addition Cu is used as a catalyst in the production of Fluidized Bed Reactor polysilicon. Titanium is a slow diffuser and easily forms oxides at high temperature, therefore its in-diffusion is unlikely. However, if present in the molten silicon (e.g. from the polysilicon, crucible, silicon nitride coating, etc.) it can be incorporated in the silicon ingot, from where it can not precipitate or be gettered, and therefore is very detrimental to the minority charge carrier lifetime. Essentially, these impurities exhibit a wide range of physical properties (e.g. diffusivity, solubility, segregation coefficient, etc.). Therefore the extent of precipitation and gettering are expected to be significantly different, and this group of metals can be considered as model impurities for the behavior of other impurities with similar characteristics.

It is important to note that in this study, the impurities are introduced in the silicon charge and are, of course, subject to a similar thermal history and process as would be any impurity in the feedstock. The thermal history of the material determines, among other aspects, the fraction of impurities which are electrically active in the Si, the properties of precipitates, etc, and thus the final impact of impurities on the solar cell performance. Therefore, the behavior of impurities in our study, including interactions of impurities with extended defects like dislocations, grain boundaries or precipitates, is as close as possible to the behavior of impurities during the entire solar cells manufacturing value-chain. Our experimental approach differs from several previous studies (e.g. in ^[3]) where impurities were introduced by ion implantation or intentional surface contamination at the wafer level, followed by a thermal anneal of the wafer.

We discuss in this article the impact on solar cell performance, while a separate article describes the segregation coefficients of the impurities and the interaction between impurity and the crystallization process causing an increased concentration of extended crystal defects^[4] (e.g. grain boundaries and highly dislocated areas). We believe our studies are representative and useful for assessment of the impact of unwanted impurities in feedstock and crystallization materials (e.g. crucible, Si₃N₄ coating, construction material, etc.).

2. Background

Comparisons Westinghouse model/study with this model/study:

In the 1970's a thorough investigation on the impact of impurities was carried out as part of the Low Cost Solar Array (LCSA) project, a.k.a. the "Westinghouse study". This investigation, carried out on Czochralski (Cz) ingots, examined a very wide range of impurities. The main differences between the LCSA investigation and the investigation carried out in this project are listed in **Tab. 1**.

Table 1. Main differences between the studies performed in the Low Cost Solar Array (LCSA) project and in the CrystalClear (CC) project.

	LCSA	CC
Crystallization	Cz (mainly mono, some multi)	Bridgman (Directional Solidification)
Resistivity p-type	3.5 Ω×cm	1.2 Ω×cm
Cell thickness	275 μm	185 μm
Cell structure	No ARC, no BSF	SiN _x , Al-BSF
Area	1 cm ²	156 cm ²
Average efficiency	9.5% (14.1% with ARC)	15.5%
reference ingot	on mono	on multi
Fabrication/optimization	no optimization, high reproducibility	
Cell process	Lab state of the art ~1978	Industry state of the art ~2008
Device model	Analytical solution of transport equations for a single wavelength	Numerical solution of the transport equations PC1D ²²
Data	Efficiency versus wafer impurity concentration, k_{eff} determined by NAA and SSMS	Efficiency versus added impurity concentration, no intermediate parameter

Anti Reflecting Coating (ARC), Neutron Activation Analysis (NAA), Spark Source Mass Spectroscopy (SSMS)

Among the most important of these are that the data reported here refers to a modern, state of the art industrial screen-print solar cell process,^[5] and that the impact of impurities is investigated on directionally solidified multicrystalline material, as opposed to Czochralski silicon ingots. In this work the direct relationship between impurities in the feedstock and the final solar cell performance is reported and analyzed. This provides the most straightforward and meaningful interpretation, especially addressed at specifying feedstock impurity tolerances. Our conclusions, therefore, do not rely on impurity analysis or estimated segregation coefficients. By comparison, the previous Westinghouse studies reported the impurity concentrations in the wafers, determined by the effective segregation coefficients, versus the solar cell performance.

In addition, in this study the total ingot height, which corresponds to 100% of the melt weight, has been used for the evaluation, as opposite to one section analyzed in

the LCSA project. Therefore, each ingot provides a broad range of impurity concentration levels of interest.

The model used here takes into consideration the distribution of impurities along the ingot height. To extract the model parameters, the entire sets of data along the ingot height 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.

3. Method

The concentration of impurities in commercially available silicon wafers is usually too low to be detected with commonly available techniques, and unintentional contamination during the sample preparation increases the possibility of measurement artifacts. In addition, it is quite difficult to obtain material with a significant variation of one specific impurity alone, or a specific combination of impurities, with the aim of identifying their impact. For these reasons we intentionally contaminated silicon feedstock with known amounts of single impurities as described in **Tab. 2**.

Table 2. *Ingot descriptions. The boron and the impurity have been introduced in the silicon charge, exception for titanium which was added after complete silicon melting.*

Element added	Label	Boron (ppm wt) (ppma)	Concentration added (ppm wt) (ppma)
-	Ref (2x)	0.13 (0.34)	Reference
Fe	Fe 50 [a]	0.13 (0.34)	53 (27)
	Fe 200	0.13 (0.34)	200 (101)
	Cr 4	0.13 (0.34)	4.08 (2.20)
Cr	Cr 40	0.13 (0.34)	40.4 (21.8)
	Cr 200	0.13 (0.34)	200 (108)
Ni	Ni 40	0.13 (0.34)	36.7 (17.6)
	Ni 200	0.13 (0.34)	203 (97.1)
Ti	Ti 10	0.13 (0.34)	9.3 (5.5)
Cu	Cu 100	0.13 (0.34)	97 (43)

[a] reported in [14]

Impurities change their state and concentration during the manufacturing of solar cells. The processes which mainly affect the impurities are (in processing sequence): crystallization, emitter formation, $\text{SiN}_x\text{:H}$ deposition, and metal contact formation. During these processes phenomena like impurity segregation, internal and external gettering, and bulk defect passivation change the concentration and the recombination activity of such impurities. The approach used in this work has the advantage of revealing the impurity impact along the entire production chain.

The amounts of impurities added have been chosen targeting typical levels of impurities in commercially produced directionally solidified multicrystalline silicon wafers,^[6,7] while aiming for a noticeable effect on both the wafer and cell levels in

comparison to uncontaminated reference material. An equilibrium segregation coefficient for this selection was assumed.^[1]

The prepared contaminated feedstock has been used to produce ingots in a small scale Bridgman-type Crystalox DS 250 furnace. This furnace allows the growth of 12 kg ingots by the directional solidification method, having a diameter of 250 mm and a height of 110 mm. The ingots were grown at Sintef in Norway. Almost all the impurities studied have been introduced together with the feedstock before the melting takes place. Titanium was the only exception, due to its affinity to react with oxygen and form a wide range of oxides. In order to reduce their formation, titanium was added to the melt after complete melting was detected.

Together with the chosen metal impurity, boron was added targeting a base p-type doping level of about $1 \Omega \times \text{cm}$ (See Tab. 2).

In order to minimize and, even more importantly, to control any unintentional contamination, the following precautions have been adopted for the ingot solidification:

1. prime quality polysilicon feedstock;
2. electronic grade crucible^[8] made of fused quartz;
3. purified silicon nitride coating as described in ref ^[9].

The unintentional contamination of each ingot, though minimal, can be considered to be approximately the same. Two reference ingots without any addition of impurities have been grown in the same conditions. The reference ingots gave an average as-grown minority carrier lifetime of about 60 μs in the middle of the ingot. This level is typical for high-quality commercial multicrystalline material. In this condition the added impurity acts like a perturbation (in most cases large) of the “normal” contamination levels. This allows studying them when in combination with a background level of impurities without a significant interaction.

Impurities can interact with each other^[10] reducing their overall impact. In this way their impact is no longer simply a linear combination of the single impurities. In this paper we study the impact of single impurity and we leave the impact of impurity combinations to a future publication.

The levels of interstitial oxygen and substitutional carbon in the as-grown wafers were approximately $8 \pm 2 \text{ ppma}$ and $2 \pm 2 \text{ ppma}$, respectively as measured by FT-IR^[11], which is in the concentration range of typical commercial multicrystalline ingots.

A selection of 200 μm thick wafers, from about 10 positions from the bottom to the top of the ingots, was subject to the p-type solar cell process. The solar cell process is the state of the art industrial process including P-diffusion, Al-Back Surface Field (BSF) $\text{SiN}_x\text{:H}$ firing through as described in Ref ^[5].

The same process has been applied to the contaminated material as well as to reference material. No process optimization has been carried out for the contaminated ingots since for this investigation we are studying the impact of the impurities on a stable reference cell process. For this reason this investigation might be more restrictive in terms of allowed impurity levels. Indeed the contaminated ingots might benefit from improved processing (e.g. optimized gettering either

external or internal and optimized hydrogenation)^[12] depending on the impurity species present.

Throughout this paper, we use the notation Xx-YY to identify the different ingots, where Xx represents the element and YY the amount added to the feedstock. For example Cr 40 refers to the multicrystalline silicon ingot intentionally contaminated with 40 ppm wt of chromium.

Results of the ingot with 50 ppm wt of iron have been reported in Ref ^[14], however for completeness and comparison some results from this ingot are also reported in this paper.

4. Results and discussion

4.1 Impact on the solar cell efficiency

In **Fig. 1**, the efficiencies of the solar cells produced from wafers of the contaminated ingots are shown as a function of the ingot height. For all contaminated ingots, the solar cell performances are best and in some case comparable to the reference uncontaminated solar cells in the range of 40-70% of the ingot height. Roughly, the efficiency results of the contaminated ingots can be divided into 3 regions: a bottom region up to 40% where the efficiency is lowered, a middle region from about 40 to 70% where the performance is best, and a top region above 70% of the ingot height where again the efficiency decreases towards the top.

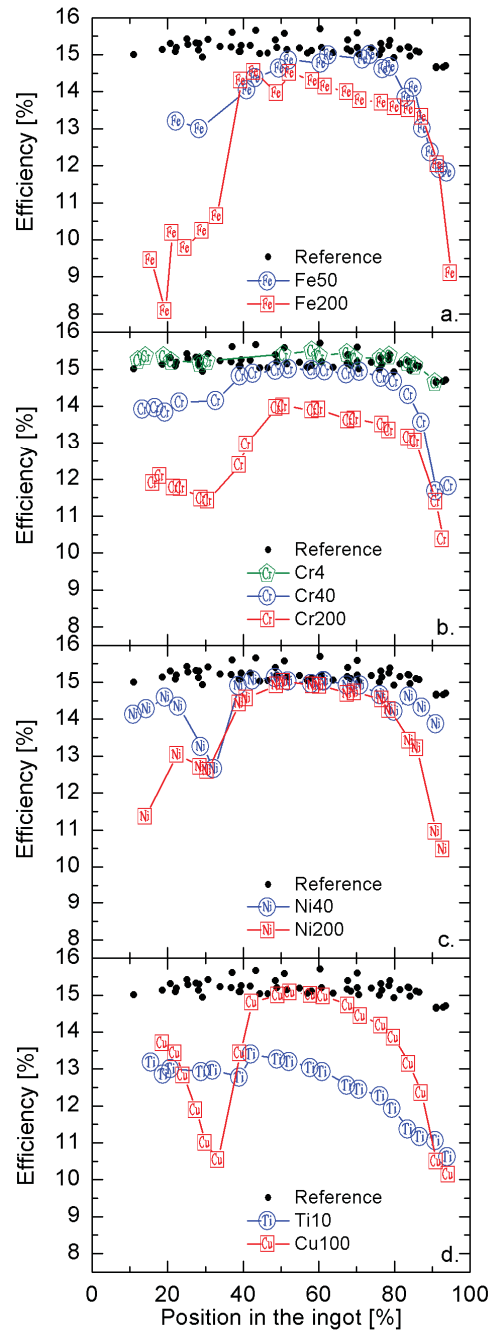


Figure 1. Solar cell efficiency versus position along the ingot height from the bottom. 1. Ingots contaminated with 50 and 200 ppm wt of iron. 2. Ingots contaminated with 4, 40 and 200 ppm wt of chromium. 3. Ingots contaminated with 40 and 200 ppm wt of nickel. 4. Ingots contaminated with 10 ppm wt of titanium and 100 ppm wt of copper.

The efficiency reduction in the bottom and on the side of directionally solidified multicrystalline ingots is a known effect^[13] due to the contact of the ingot with the crucible and the Si_3N_4 coating. The efficiency reduction observed in the bottom of the contaminated ingots is more extended than in the reference ingot (below 10% of the ingot height). The cause for this extended degradation near the bottom cannot be related to the in-diffusion of impurities from the crucible or coating, since approximately the same conditions (e.g. melting time, crystallization time and cooling down) has been applied for the casting of all the ingots. Indeed a poorer crystallographic structure has been reported^[14] in the ingot Fe 50 ppm wt in comparison to the reference ingot. Smaller grains and highly dislocated areas were found in the bottom and top of the ingot. In this study we found that the degradation in the bottom increases with the impurity level in the feedstock (see Fig. 1). In addition to iron this degradation is visible for chromium, nickel and copper. In the case of titanium the efficiency degradation is so large that it is difficult to discriminate a possible bottom effect from the segregation effect. However, this does not always correspond to an increase in the crystallographic defect density.^[15]

The performance degradation in the top of the ingot is a well known effect as well. During the crystallization impurities segregate into the molten phase. 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 10x higher concentration of impurities is 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.

In addition immediately after crystallization completion and during the cooling down the impurities diffuse back from the top, spreading their concentration. This phenomenon is limited by the cooling down rate and impurity diffusivity to a small fraction of the ingot height.

The efficiency reduction observed in the top of the contaminated ingot can therefore be explained by the combination of these effects. If the degradation in the reference ingot is visible at 99% of the ingot height, an ingot with 10x more impurity concentration shows this degradation at 90% and so forth. In the next section we describe a model based on the segregation of impurities to verify that indeed segregation is the leading mechanism which explains the degradation trend towards the top of the ingots

4.2 Impact on the internal quantum efficiency

In order to understand the degradation mechanisms observed and their causes, the internal quantum efficiency (IQE) of the solar cells has been calculated from spectral response and reflectance measurements (see Fig. 2 as an example for the ingot with Ti 10 ppm wt). In Fig. 3 the relative IQEs at 400 nm and 1000 nm compared to the reference ingot at the respective wavelength are shown for each contaminated ingot as a function of the ingot position from the bottom to the top. We chose to report the IQEs only at these wavelengths for clarity of the figures.

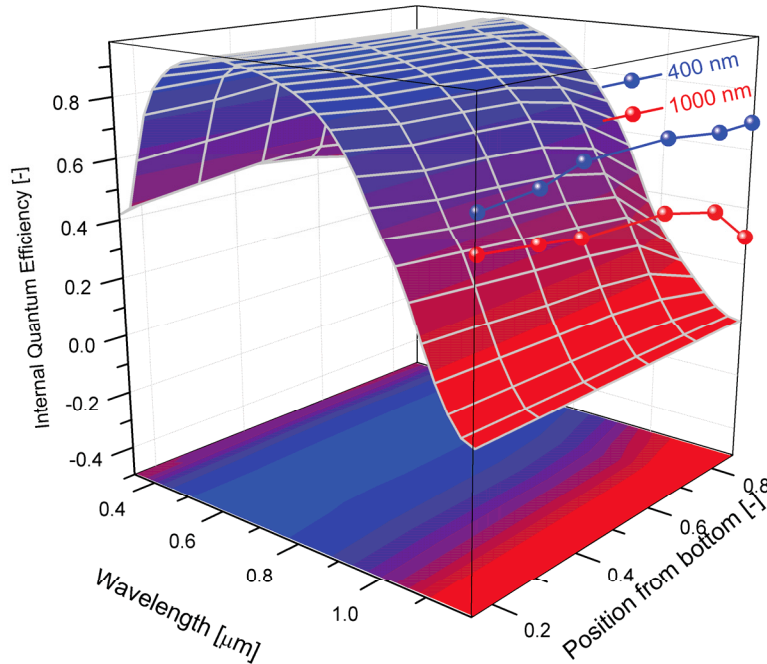


Figure 2. IQE versus wavelength and position in the ingot for the ingot with 10 ppm wt of titanium. The IQE at long wavelength (e.g. 1000 nm) decreases towards the top of the ingot. The inset shows the IQE at 400 nm and 1000 nm, which are related to the emitter recombination and the base recombination, respectively.

The IQE at 400 nm gives information on the emitter recombination due to the shallow absorption of these photons in silicon. Below 400 nm the absorption in the SiN_x anti reflecting layer needs to be taken into consideration, complicating the analysis unnecessarily.

On the other hand photons with a wavelength of 1000 nm are absorbed deeply in the silicon wafers. Therefore, IQEs at this wavelength are linked to the minority carrier diffusion length as well as to the rear surface conditions in terms of both passivation and reflection. Since a highly reproducible solar cell process has been applied and assuming that the properties of the rear surface are not changed by the presence of impurities, the IQEs variation at 1000 nm are directly linked to variations in the base-bulk recombination. On the other hand, if the impurities do interact with the rear surface (e.g. degrading the surface passivation) the IQE at 1000 nm will be reduced, resulting in an overestimation of the base-bulk recombination. However, such an interaction is unlikely, and so we interpret the IQE at 1000 nm to be related only to base-bulk recombination.

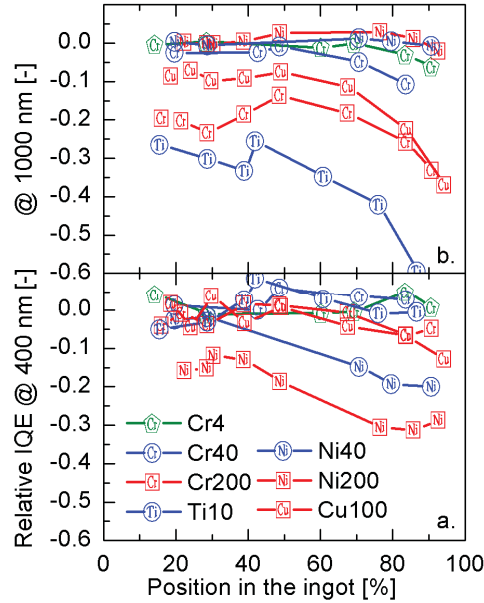


Figure 3. Relative internal quantum efficiency versus position in the ingot from the bottom at a wavelength of 400 nm (a.) and 1000 nm (b.). The IQE at 400 nm represents the recombination in the emitter region while the IQE at 1000 nm represents the recombination in the base-bulk. Chromium, iron (not shown) and titanium reduce the IQE at long wavelength (1000 nm). Nickel reduces the IQE at short wavelength (400 nm). Copper reduces the IQE at long as well as short wavelength.

Iron, chromium and titanium lead to an increase in the base-bulk recombination. The base-bulk recombination scales with the impurity level as expected. In addition it increases with the ingot height as expected considering the segregation of impurities into the liquid phase during the crystallization. The ingot with 50 ppm wt of iron shows such an increase also in the bottom, while in the ingot with 200 ppm wt this effect is present but masked by the lower IQE at 1000 nm along the overall ingot.

These impurities do not lead to any increase of the emitter recombination along the overall ingot. This suggests that even in the very top of the ingots the high concentration of Fe, Cr, and Ti does not affect the emitter recombination at least to levels that the solar cell performances are reduced. Despite the fact that gettering to the emitter is very effective for e.g. Fe and Cr, as evident from the negligible impact of such impurities in the middle of the ingot, the accumulation of atoms in the emitter region does not cause additional noticeable recombination.

Nickel does not show an increase in the base-bulk recombination. Even the highest concentration introduced in the feedstock (200 ppm wt) does not cause a visible effect at long wavelengths. Therefore its effect on the base-bulk recombination can

be considered a second order effect. On the other hand, the IQE at 400 nm decreased in both the Ni contaminated ingots. The reduction increases towards the top of the ingots due to the impurity segregation in the liquid phase confirming that this effect is indeed caused by the presence of nickel, and it scales with its concentration as well.

Copper shows an increase in the base-bulk recombination towards the top of the ingot in a similar way to Fe, Cr and Ti. However an increased recombination in the emitter especially in the top of the ingot is also observed.

Nickel and copper are both fast diffusing transition metals. During wafer cooling, even without the presence of a phosphorus diffusion, nickel and copper become supersaturated and diffuse to the wafer surfaces where they form precipitates. On the other hand atoms which cannot reach the surfaces form precipitates in the bulk. The reason for copper to influence the base-bulk recombination might be related to the higher solubility (see Table 3) of Cu with respect to Ni (about 1 order of magnitude). In addition Cu preferentially forms metal rich precipitates Cu_3Si which do not fit well in the Si lattice, as opposed to the silicon rich precipitates of Ni (NiSi_2) which present a better fit. Due the misfit of copper precipitates, more silicon self interstitials are emitted, therefore copper precipitates are decorated with an extended extrinsic dislocation network^[16] potentially resulting in higher bulk recombination.

4.3 Impact on the solar cell fill factor

The recombination in the base as well as in the emitter reasonably explain the degradation of the contaminated ingots, however the large effect in the bottom and in the very top is not yet completely accounted for. The fill factor (FF) decrease is another mechanism that plays a role in the (further) decrease of the solar cell performance. As shown in Fig. 4, the FFs of the solar cell are significantly reduced in the bottom and in the very top of the ingots contaminated at high and medium concentrations. These solar cells are mainly affected by the presence of shunts. The FF limitation due to the link with the V_{oc} as reported by Green^[17] and the minority carrier injection level dependency as calculated by Macdonald et al.^[18] play a secondary order effect here.

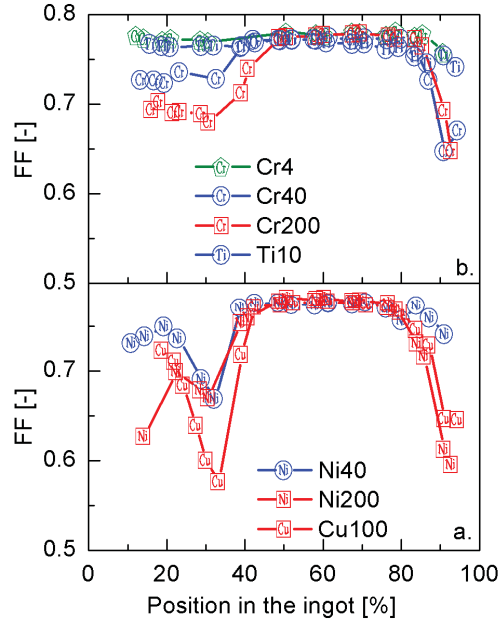


Figure 4. Fill factor versus position in the ingot. Top ingots contaminated with chromium, iron and titanium. Bottom ingots contaminated with nickel and copper.

In the case of chromium, there is hardly any distinction in the FF degradation in the top between the two ingots with 40 and 200 ppm wt. Iron also shows almost no difference between 50 and 200 ppm wt concentrations in the top. In Cr 4 ppm wt the FF is similar to the reference uncontaminated ingot along the overall ingot.

In the case of nickel the reduction in the top of the ingot with 40 ppm wt is very limited in comparison to the ingot with similar amount of Cr. In this case, we have to consider that the atomic concentration in the melt for nickel is about 20% less than chromium (due both to the different concentration and the different atomic weight). An exception is for the ingot with Ni 200 ppm wt, for which the FF has a deeper impact from the top in comparison to the ingots with same amount of both Cr and Fe. It is interesting to note that copper with 100 ppm wt has a FF degradation deeper from the top in comparison to both Cr and Fe with 200 ppm wt, in similarity to nickel. The impact of 10 ppm wt of Ti is much smaller towards the top in comparison to Fe and Cr with 40 ppm wt despite the larger degradation observed in the efficiency.

The FF degradation in the bottom of the ingots is not visible in ingots containing less than about 10 ppm wt (e.g. chromium and titanium). Instead, above 40 ppm wt the degradation is visible and scales with the impurity concentration differently from what is observed in the top. The onset for the degradation in the bottom should be in the range 10-40 ppm wt.

In conclusion the onset for the FF degradation is in first approximation dependent on the amount of impurities introduced rather than on their species. For both Cr and Fe a similar FF degradation trend is visible at both medium (40-50 ppm wt) and high (200 ppm wt) concentrations, indicating that a kind of saturation on the FF reduction is reached.

The exception is for nickel where the degradation at 200 ppm wt starts at a lower height than for Cr and Fe at the same concentrations. The different behavior of Ni, and to some extent Cu, can be explained by their fast diffusivity in silicon which is also responsible for the reduced IQE at short wavelength. As fast diffusers they can easily out-diffuse during cooling down forming precipitates at the wafer surfaces. The presence of such precipitates in the emitter region can cause additional shunts which can be responsible for the greater FF reduction observed at high concentration (i.e. Ni 200 ppm wt and Cu 100 ppm wt). On the contrary, at lower concentration, i.e. Ni 40 ppm wt, the FF degradation might be related to the same mechanism affecting Cr and Fe (see next paragraph) since the smaller size of such precipitates does not cause the additional shunts observed in Ni 200 ppm wt.

In order to outline the mechanism that affects the FF degradation, images of these solar cells have been taken using lock-in thermography.^[19] The shunts revealed by this technique are mainly located along grain boundaries (GBs). The shunt areas have been analyzed on neighboring wafers by means of scanning electron microscopy and energy-dispersive X-ray spectroscopy. In the shunt location we found the presence of filaments and sheets coming out from the GBs and containing nitrogen. The relation between SiN and SiC inclusions with the shunt is well documented in the literature.^[20] Here it is important to note that, despite the large concentration of impurity, the cause of the severe shunt is directly related to the presence of nitrogen rather than to the impurity itself. The impurity might have nucleated the formation of such a filament or rod.^[21] This can explain why the shunt is visible in the ingot with high and medium concentration of impurities.

The appearance of this phenomenon in the bottom of the ingot might be aggravated by the geometry of the small lab scale furnace that was used to cast the ingots and by the use of crucibles with a spherical bottom. Circular areas in the diffusion length maps^[14] with increased crystal defects, which are centered on the original ingot centre, point in this direction.

The cause of these shunts is not well understood and the interpretation of these issues will need a dedicated study and most likely an adaptation of the crystallization process.

In the next section we describe a model based on the segregation of impurities to verify that this is the leading mechanism which explains the degradation trend observed at the top of the ingots.

5. Modeling

The impurity impact model described in this section was derived to understand the main physical phenomena which contribute to the solar cell performance degradation along the ingot. In addition, the model provides a means to predict the behavior of solar cells manufactured from silicon containing known concentrations

of impurities. The aim is also to define a unique parameter to quantify the ‘dangerousness’ of each impurity. In the first part we base the model on the degradation due to the reduction in the base-bulk lifetime for iron, chromium and titanium while in the second part the emitter-bulk recombination is taken into account to model the behavior of nickel. In the third part the combination of the two effects is considered to model copper. The Scheil distribution of impurities along the ingot is the common mechanism considered in all the models.

5.1 Base bulk recombination

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

$$N_t = \alpha C_s \quad (1)$$

- 3) The minority carrier lifetime in the base-bulk can be described by:

$$\frac{1}{\tau_b} = \frac{1}{\tau_{\text{imp}}} + \frac{1}{\tau_{\text{other}}} = v_{\text{th}} \sigma_n N_t + \frac{1}{\tau_{\text{other}}} \quad (2)$$

where $1/\tau_{\text{imp}}$ is the recombination due to the element intentionally added which is proportional to the concentration N_t of electrically active impurities at low injection level, and $1/\tau_{\text{other}}$ is the recombination due to other defects (i.e. not caused by the intentionally added impurity). v_{th} is the thermal velocity of the charge carrier, 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-bulk. The solar cell performance as a function of the base-bulk lifetime has been modeled using PC1D^[22], a software dedicated to the numerical solution of the transport equations.

Assumption 1) has been verified by neutron activation analysis as reported in Ref^[23]. The electrical activity is influenced by phenomena like precipitation, gettering and hydrogenation. Therefore the proportionality constant (α) is element dependent and is a global parameter since it correlates the electrical activity at the end of the solar cell process with the total initial solid impurity concentration. In Eq. 2 we discriminate between recombination due to the addition of the target impurity and the recombination via defects already present in the material (e.g. unintentional contamination, grain boundaries, dislocations etc.). We use the reference ingots (not intentionally contaminated) as an estimate for $1/\tau_{\text{other}}$. We assume here that the impact of the added impurity results in recombination which is proportional to the concentration of the added impurity. In the case where the dissolved impurity dominates the recombination (i.e. negligible impact of extended crystallographic defects and precipitates), σ_n is the minority carrier capture cross section of the point defect. Otherwise this parameter represents an ‘effective’ minority carrier capture cross section of the dominant extended defect (e.g. precipitates, etc.).

defect. Otherwise this parameter represents an 'effective' minority carrier capture cross section of the dominant extended defect (e.g. precipitates, etc.). The impact of the impurities on the FF cannot be modeled with a one dimensional model since the FF is mainly limited by shunts which have a spatial distribution and involve the interaction 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 $k_{eff} \times \sigma_n \times \alpha$.^[24] C_0 is the concentration of added impurity in the feedstock. In **Fig. 5**, **Fig. 6**, and **Fig. 7**, the fit of the model with the raw data is shown for the ingots Cr 40 ppm wt, Fe 50 ppm wt and Ti 10 ppm wt. The model fits the experimental data trend very well along the ingot height. An exception is in the bottom of the Fe 50 ppm wt ingot, since the degradation in the bottom is not taken into consideration in the model.

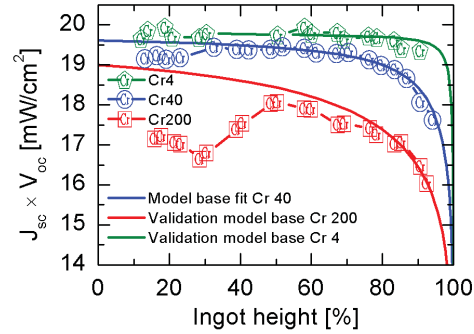


Figure 5. Short circuit current times open circuit voltage versus position in the ingot from the bottom for the ingots contaminated with chromium. The model used is based on the degradation of the base-bulk recombination. The parameter fitting has been carried out on the ingot with 40 ppm wt of chromium obtaining an excellent fitting. The model has been validated using the ingots with 4 ppm wt and 200 ppm wt.

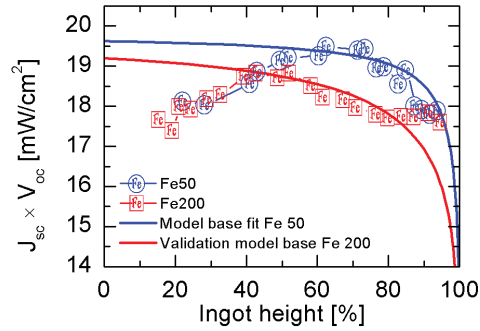


Figure 6. Short circuit current times open circuit voltage versus position in the ingot from the bottom for the ingots contaminated with iron. The model used is based on the degradation of the base-bulk recombination. The parameter fitting has been carried out on the ingot with 50 ppm wt of iron obtaining an excellent fitting. The model has been validated using the ingot with 200 ppm wt obtaining a good fitting of the data up to 85% of the ingot height.

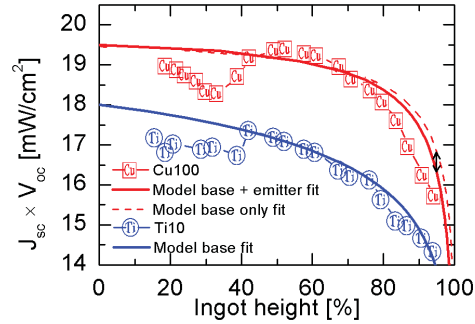


Figure 7. Short circuit current times open circuit voltage versus position in the ingot from the bottom for the ingots contaminated with titanium and copper, separately. Titanium: The model used for titanium is based on the degradation of the base-bulk recombination. An excellent data fitting has been obtained. Copper: The model using only the base recombination overestimated the performance in the top (dash line) for copper. A better model is based on the degradation of the emitter-bulk recombination and the base-bulk recombination together. A relatively good data fitting has been obtained (solid line).

The distribution of impurities according to the Scheil equation is the dominant mechanism explaining the solar cell degradation trend 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 phosphorous 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. GBs and highly dislocated areas) as reported in Ref ^[14]. Indeed the gettering effectiveness is known to be influenced by the presence of dislocations. ^[25]

In order to validate the model, the same fitting parameter of Cr 40 ppm wt has been used to fit the data from the ingots with 200 ppm wt and 4 ppm wt of chromium by changing only the added Cr concentration (C_0). The model prediction both for 200 ppm wt and 4 ppm wt overlay perfectly the experimental data (see Fig. 5). An exception occurs in the bottom of the Cr 200 ppm wt ingot, since the degradation there is not taken into consideration in the model. Since the effect in the bottom is visible only for higher concentrations of impurities, the model gives a good prediction for medium to low concentration levels along the entire ingot length. A similar validation has been attempted for the ingot with 200 ppm wt of Fe. It is visible in Fig. 6 that the model overlaps the experimental data in the range 40 to 85% of the ingot height. A deviation is observed above about 85% where the model is overestimating the impact of Fe on the solar cell performance. To understand this deviation we have to consider that this validation method assumes that the electrical activity α of the impurity is constant independently from the concentration of impurities. In the case of the ingot Fe 200 ppm wt an electrical activity of 4% has

been found^[23] on as grown wafers from the ratio between interstitial and total Fe in comparison to an electrical activity of 10% found for Fe 50 ppm wt.^[14] This factor two difference in the electrical activity, even on as grown material, could explain the deviation in the top of the ingot. A thorough fitting of the data of Fe 200 ppm wt ingot cannot be achieved due to the relatively flat profile of the $J_{sc} \times V_{oc}$ product along the ingot.

In the model shown the simulation of the J_{sc} and the V_{oc} separately have a maximum discrepancy of about 1% or less.

It is relevant to compare the value of α for each impurity since it reveals information about the ability of the ingot growth and solar cell processes to reduce the detrimental effect of the impurities by means of e.g. precipitation, gettering and hydrogenation. This parameter is not directly a fitting parameter since the product $k_{eff} \times \sigma_n \times \alpha$ is actually fitted. The effective segregation coefficient k_{eff} has been measured by means of Neutron Activation Analysis (NAA).^[23,26] It is possible to then estimate α by assuming that the dissolved impurity dominates the recombination, and therefore σ_n is the minority carrier capture cross section of the point defect. This assumption is not completely fulfilled since at higher concentration levels (e.g. in the top or for ingots with high added impurity level) the impurity interacts with the crystallographic structure increasing the crystallographic defects^[14,23] (e.g. GBs and dislocations) and therefore participating in and increasing the bulk recombination. However, to the extent of its validity (e.g. at lower concentrations) the estimation of α can give an indication of the impurity electrical activity. In **Tab. 3** are reported the values of σ_n ^[27,28,29] used to calculate α . It is evident that α is as low as 0.1% for Fe. This means that just a small amount of this impurity is active or contributes to the recombination. In the case of Cr, α is about 6% which is reasonable considering that the diffusivity is 3 times smaller and the solubility 1 order of magnitude smaller in comparison to iron. In the case of titanium, we assume that the dominant recombination occurs through the double-donor defect energy-level as proposed by Paudyal et al.^[28] This is reasonable due to the similarity between the samples investigated there and in this study (e.g. multicrystalline ingot prepared by intentional addition of Ti in the silicon melt). Using the electron capture cross section measured by Paudyal, α is as large as 90%. Indeed Ti being a slow diffuser in silicon presents hardly any getterability and precipitation. Therefore its electrical activity is expected to be close to the total atomic concentration.

We stress that the α values have been determined for a state of the art industrial-type process, as described in section 3. We demonstrate that these values of α can be actually achieved with the technology available today, and represent a benchmark. Therefore best-practice industrial production should experience similar sensitivity towards the impact of impurities. In addition, these values of α are an underestimation of what can be tolerated with future developments, since no dedicated optimization (e.g. annealing, gettering, defect passivation etc.) has been carried out for the intentionally contaminated ingots. A similar argument applies to the accepted impurity level C_L described in section 6.

5.2 Emitter bulk recombination

The addition of nickel to the feedstock did not reduce the base-bulk diffusion length at the solar cell level, as reported in the previous section. Instead, nickel has the peculiar effect of reducing the IQE at short wavelengths, which corresponds to recombination taking place in the emitter region. This recombination (also often characterized as an emitter saturation current density J_{oe}) is the combination of the emitter-bulk recombination and the surface recombination-velocity. In order to model the impact of nickel, a model for the recombination in the emitter has been produced. We model the solar cell as a base and emitter volume characterized by their bulk recombination, τ_b and τ_{be} , respectively. The base-bulk recombination is kept constant. The front-surface recombination-velocity is assumed constant as well for simplicity and further arguments for the validity of this assumption are presented below. The emitter profile has been approximated by a double error function (*erf*) based on SIMS (Secondary Ion Mass Spectroscopy) emitter profile measurements. The emitter depth is $\sim 0.3 \mu\text{m}$. The surface recombination velocity for the emitter is 10^5 cm/s and the emitter-bulk diffusion length is $\sim 1 \mu\text{m}$. With this parameter the reference solar cell has been modeled taking into consideration both the IV parameters and IQE measured. We aim to verify if the emitter-bulk recombination can explain the trend of the $J_{sc} \times V_{oc}$ product along the ingot. The model used is similar to the one described for the base-bulk recombination where Eq. 2 refers now to the emitter-bulk recombination (τ_{be} in place of τ_b , and σ_p in place of σ_n). We have to consider that, similarly to the case of base-bulk recombination, α is a global parameter which represents the fraction of impurities that contributes to the recombination in the emitter and includes phenomena like precipitation, gettering and hydrogenation. In addition, since most of the nickel in the base diffuses towards the wafer surfaces, the nickel concentration in the emitter is much higher than in the bulk, therefore α can be larger than unity and cannot be directly compared to the α estimated in the case of base-bulk recombination. We should note that N_b , σ_p and α refer to the dominant defect active in the n-type emitter. Since nickel precipitates quantitatively, this defect is quite likely to be nickel precipitates. Indeed Trushin et al.^[30] estimated a large hole capture cross section ($\sigma_p = 1 \times 10^{-11} \text{ cm}^2$) for NiSi_2 . However, since both the precipitates characteristics (e.g. size and density) and the recombination parameters of Ni are not definitely known, the electrical activity α of nickel cannot be directly determined. Nevertheless, this does not prevent an attempt to fit the data to at least verify the overall validity of the model.

To this end, the $J_{sc} \times V_{oc}$ product of the solar cell along the ingot has been fitted with the model. The only fitting parameter of the model is the product $k_{eff} \times \sigma_p \times \alpha$ (σ_p being the minority carrier capture cross section of the dominant defect). In **Fig. 8**, the fit of the model with the raw data is shown for the ingot with 40 ppm wt of nickel. The model fits the experimental data along the ingot height very well. This clearly demonstrates that the distribution of impurities according to Scheil is the dominant mechanism explaining the solar cell degradation trend along the ingot, even in the case of emitter recombination.

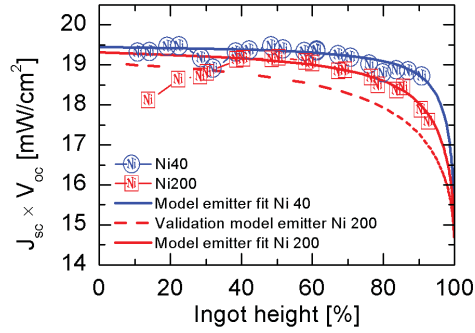


Figure 8. Short circuit current times open circuit voltage versus position in the ingot from the bottom for the ingots contaminated with nickel. The model used is based on the degradation of the emitter-bulk recombination. The data fitting has been carried out on the ingot with 40 ppm wt of nickel obtaining an excellent fitting. The model has been validated using the ingot with 200 ppm wt obtaining bad data fitting (dash line). Fitting the ingot with 200 ppm wt separately a reduced electrical activity is found (solid line).

In order to verify that indeed the emitter-bulk recombination explains the degradation of the solar cell performance, we simulate separately the J_{sc} and the V_{oc} using the same fitting parameters used to fit the $J_{sc} \times V_{oc}$ product. The V_{oc} is mainly degraded in comparison to the J_{sc} . We verify that the model predicts the behavior of these two parameters separately very well and that the V_{oc} is mainly responsible for the degradation.

In analogy to the procedure used above for the base-bulk recombination caused by Cr and Fe, we have attempted to validate the model by using the fitting parameter from the Ni 40 ppm wt ingot to then fit the data from the ingot with Ni 200 ppm wt, by changing only the added Ni concentration (C_0). The model strongly underestimates the $J_{sc} \times V_{oc}$ product of the ingot Ni 200 ppm wt along the ingot height. In order to fit the experimental data the $\sigma_p \times \alpha$ ^[31] product must be reduced by about a factor two, obtaining a good fitting. This means that the model explains the degradation trend but either the dominant defect (σ_p) or the electrical activity (α) change. The precipitation of nickel is not diffusion limited therefore one could expect that Ni precipitates grow in size reducing the electrical activity per Ni atom.

The simulations of the J_{sc} and the V_{oc} separately for Ni 200 ppm wt (using the reduced electrical activity) have a discrepancy of about 1 %. Indeed experimentally, the ingot Ni 200 ppm wt has similar V_{oc} of the ingot Ni 40 ppm wt until 80% of the ingot height while the J_{sc} degrades along the overall ingot. In the $J_{sc} \times V_{oc}$ product these two effects compensate each other explaining the good fitting obtained.

The dependence of the $J_{sc} \times V_{oc}$ on the emitter-bulk recombination is such that in the most extreme case analyzed here (8% reduction of $J_{sc} \times V_{oc}$ at about 90% of the ingot height in the ingot with 200 ppm wt) the emitter-bulk diffusion length has to be reduced from 1 μm to 0.5 μm .

In the device the presence of nickel in the emitter region might have an impact on the front-surface recombination-velocity as well as on the emitter-bulk

recombination. However, the model includes the recombination on the base emitter alone. Building a model which includes both the phenomena will unnecessarily complicate the model without adding much information. Indeed very little is known about the minority carrier capture cross section of substitutional nickel in the bulk (interstitial nickel is unstable because it out-diffuses to the surfaces) and even less is known about the surface recombination parameters. In addition, nickel precipitates massively and therefore recombination parameters for the precipitates need to be taken into account as well.

The diffusivity of nickel explains the different behavior of Ni in comparison to e.g. Fe and Cr. Getterable impurities like Fe or Cr should also increase the recombination in the emitter. The lack of this degradation for Cr and Fe is not yet understood. We can suggest that Fe has a very small minority carrier cross section in the n-type emitter layer ($7 \times 10^{-17} \text{ cm}^2$) which could explain why iron does not reduce the IQE at short wavelengths. The same argument does not apply to Cr since its capture cross section is believed to be about 2 orders of magnitude higher as reported by Schmidt.^[29] On the other hand if precipitates are dominating the recombination in the emitter, iron and chromium precipitate capture cross sections should also be small, by the same argument. Very little is known about recombination parameters of precipitates, thus this hypothesis remains unproven. It is generally accepted that the emitter recombination is in a regime limited by Auger recombination and that recombination via defect levels is a second order effect and probably one of the reason why gettering works. The large estimated capture cross section of NiSi_2 is the only evidence that precipitated Ni is extremely active and therefore the emitter goes into a Shockley-Read-Hall limited regime which could explain the degradation observed in the emitter.

5.3 Model for Cu

The addition of copper to the feedstock causes an impact on the IQE at long wavelength as well as at short wavelength, as reported in the previous section. In order to model the behavior of copper the model for the base-bulk recombination is not sufficient on its own. In **Fig. 7** it is shown that the $J_{sc} \times V_{oc}$ product in the top of the ingot is largely overestimated. This means that another recombination mechanism is active and becomes important in the region of the ingot where the concentration of copper increases. Therefore, we include in the model the recombination in the emitter-bulk too. To model the data the contribution of each of the two models (base-bulk recombination and emitter-bulk recombination) needs to be determined. Fitting the $J_{sc} \times V_{oc}$ product is not possible since it is influenced by both recombination channels. Therefore we fitted separately the IQEs at 400 nm and 1000 nm with the model for the emitter-bulk recombination and the base-bulk recombination, respectively. The two fitting parameters, one for each type of recombination, are the products $k_{eff} \times \sigma_p \times \alpha$ and $k_{eff} \times \sigma_n \times \alpha$ as described for the two separate models. The results of the two fittings are then given as input to PC1D^[22] to calculate the $J_{sc} \times V_{oc}$ product of the combined recombination. A tentative better fitting is visible at higher ingot height as seen in Fig. 7.

6. Accepted impurity level

The effect of impurities like Fe, Cr, Ti, Ni and Cu has been modeled and the fitting parameters have been estimated. We use the model 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. We define C_L as the limiting concentration of impurities in the molten silicon charge which results in a $J_{sc} \times V_{oc}$ product with about 2% relative degradation with respect to the reference uncontaminated ingot up to 90% of the ingot height. Each impurity has a characteristic value of C_L . 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 along the ingot. It therefore represents a true measure of impurity impact. The higher the C_L value, the lower is the impact on solar cell level.

We estimate C_L for all the impurities we have modeled as shown in Tab. 3. The results is that 8 ppm wt of Cr, 11 ppm wt of Fe or 0.1 ppm wt of Ti are all equivalents in terms of solar cell performances. In the case of nickel 13 ppm wt is found for the ingot Ni 40 ppm wt and 30 in the case of ingot Ni 200 ppm wt. This is due to the different electrical activity at higher concentration as reported in the model section. The former limit (13 ppm wt) should be better considered since more restrictive and since it is inferred from ingot Ni 40 which has a contamination closer to this limit than ingot Ni 200. Copper results in a C_L value of 8 ppm wt like chromium and similar to iron. This is quite unexpected since copper is believed to have a weaker impact on the cell performance than other impurities mainly due to its large diffusivity. However, we need to consider that the segregation coefficient of copper^[1] is about two orders of magnitude higher than iron.

Only if a single element is present and other sources of contamination (e.g. crucible, Si_3N_4 coating, etc.) provide a negligible contribution, this value can roughly be approximated to the allowed concentration of impurities in the feedstock. Note that interactions between impurities can cause a non linear behavior which complicates the estimate in the generic 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. 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 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 which can be easily compared. We stress that C_L has been determined by modeling a state of the art industrial-type process, as described in section 3. In addition, the results represent an underestimation of what can be achieved with future development since no dedicated optimization (e.g. annealing, gettering, defect passivation etc.) has been carried out for the intentionally contaminated ingots.

The importance of C_L is relevant not only from the feedstock point of view. Impurity contaminations can come from other sources as well, for example the purity of the crucible and Si_3N_4 coating.^[32] In addition, the construction materials and the use of catalysts or reducing agents for the fabrication of the feedstock as well as the ingot

casting equipments represent a known source of silicon contamination. Therefore it is a fundamental issue for the further development of photovoltaics to accurately ascertain the impact of such impurities.

Table 3. Impurity electrical activity and impurity limit calculated for each impurity. Also shown are the effective segregation coefficients and minority carrier capture cross sections used in the calculation of the electrical activity.

Impurity	Diffusivity @ RT and 850 °C [16] [cm ² /s]	Solubility @ 850 °C [16] [cm ⁻³]	Effective segr. coeff. [2326] k_{eff} [-]	Minority carrier capture cross section σ_n [cm ²]	Electrical activity α [%]	Impurity limit [a] - (fitting ingot used) C_L [ppm wt] (ppma)
Cr	(2×10^{-19}) (3.6×10^{-7})	(1.7×10^{12})	3.1×10^{-6}	$\sigma_{nCr} = 4.5 \times 10^{-15}$ [29]	5.9	8 (4.3) - Cr40
Fe	(4×10^{-15}) 1.2×10^{-6}	(1.2×10^{13})	1.5×10^{-5}	$\sigma_{nFe} = 4 \times 10^{-14}$ [27]	0.11	11 (5.5) - Fe50
Ti	(3×10^{-36}) 7.6×10^{-11}	(1.7×10^{10})	3.5×10^{-5}	$\sigma_{nTi} = 1.5 \times 10^{-15}$ [28]	93	0.11 (0.065) - Ti10
Ni	(2×10^{-11}) 1.6×10^{-5}	3.5×10^{16}	-	-	-	13 (6.2) - Ni40 30 (14) - Ni200
Cu	(1×10^{-9}) 8.0×10^{-5}	(1.1×10^{17})	-	-	-	8 (3.5) - Cu100

[a] Performance degradation of about 2%_{rel} at 90% of the ingot height

(..) Diffusivity and solubility value extrapolated to temperatures beyond the validity region

7. Conclusions

The impact of impurities on solar cell performance has been investigated. The transition metals iron, chromium, nickel, titanium and copper have been considered in this study. Each impurity has been intentionally added to the silicon feedstock used to grow p-type directionally solidified multicrystalline silicon ingots. The contamination levels are chosen targeting typical levels of such impurities in silicon ingots while aiming for a noticeable effect on both wafer and cell level in comparison to uncontaminated reference material. A state of the art screen-print solar cell process has been applied to wafers cut from the ingot from the bottom to the top. The obtained solar cells have been characterized and compared to reference uncontaminated solar cells to correlate the cell performance with the impurity contamination levels. Adding 50 ppm wt of iron or 40 ppm wt of nickel or chromium to the silicon feedstock results in equivalent solar cell performances compared to the reference in the range of 40 to 70% of the ingot height. Addition of 10 ppm wt of titanium dramatically reduces the efficiency along the entire ingot. Impurities like iron, chromium and titanium cause a reduction in the wafer diffusion length. Nickel does not have an impact on the diffusion length even at the highest concentration used in the feedstock (200 ppm wt). On the other hand nickel affects strongly the emitter recombination reducing significantly the solar cell performance. Copper has the peculiarity to impact both the base-bulk recombination as well as the emitter-bulk recombination.

Two models have been derived to fit the degradation along the entire ingot based on the Scheil distribution of impurities. The solar cell performance has been modeled as a function of the base-bulk recombination and the emitter-bulk recombination. The models fit the experimental data very well. The models have been also successfully

validated using ingots with different concentration levels of impurities. Unexpectedly, the Scheil distribution of impurities along the ingot leaves its fingerprint also at the end of the solar cell process. A measure of impurity impact has been defined as the level of impurity which causes a degradation of about 2% up to 90% of the ingot height. This directly relates the added concentration of impurities to the solar cell performance and it is not affected by the knowledge of the effective segregation coefficient, the capture cross section and the electrical activity individually, since only their product is the fitting parameter used in the model. The result is that 8 ppm wt of Cr, 11 ppm wt of Fe, 0.1 ppm wt of Ti, 4 ppm wt of Ni or 8 ppm wt of Cu are all equivalents in terms of solar cell performances. The advantage of this parameter is that it comprises the different impurities physical characters in one single parameter which can be easily compared.

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4.3

Effect of Iron in Silicon Feedstock on p- and n-type Multicrystalline Silicon Solar Cells

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Abstract: The effect of iron contamination in multicrystalline silicon ingots for solar cells has been investigated. Intentionally contaminated *p*- and *n*-type multicrystalline silicon ingots were grown by adding 53 parts per million by weight of iron in the silicon feedstock. They are compared to reference ingots produced from non-intentionally contaminated silicon feedstock. *p*-type and *n*-type solar cell processes were applied to wafers sliced from these ingots. The as-grown minority carrier lifetime in the iron doped ingots is about 1-2 μ s and 6-20 μ s for *p*- and *n*-type, respectively. After phosphorus diffusion and hydrogenation this lifetime is improved up to 50 times in the *p*-type ingot, and about 5 times in the *n*-type ingot. After boron/phosphorus co-diffusion and hydrogenation the improvement is about 10 times for the *p*-type ingot and about 4 times for the *n*-type ingot. The as-grown interstitial iron concentration in the *p*-type iron doped ingot is in the order of 10^{13} cm⁻³, representing about 10% of the total iron concentration in the ingot, and is reduced to below 10^{11} cm⁻³ after phosphorus diffusion and subsequent hydrogenation. The concentration of interstitial iron after boron/phosphorus co-diffusion and hydrogenation is about 10^{12} cm⁻³, pointing out the reduced gettering effectiveness of boron/phosphorus co-diffusion. The effect of the iron contamination on solar cells level is a decrease of the diffusion length in the top half of the ingots, with a trend in agreement with Scheil's model for segregation. This is, however, not the only impact of the iron. An increased crystal defect concentration in the top and bottom of the Fe doped ingots, compared to the reference ingots, is observed, which contributes considerably to the degradation of the solar cell performance.

1. Introduction

The research performed in the 1980's by Westinghouse Corp¹ is still used as reference for the effect of impurities on solar cell performance. However, because of the modifications of cell processes since then, and the increased use of multicrystalline cast ingots instead of single-crystalline ingots, there is a need for updated and more detailed studies.

Also, the earlier work of Westinghouse focussed on solar cell efficiency. The minority carrier diffusion length on solar cell level was not directly measured but it was approximated by modelling of results. The diffusion length as a function of impurity concentration is the most reliable input parameter to model and predict impact in different cell architectures (e.g., different thickness, different surface passivation, etc.).

In this work we study the impact of Fe intentionally introduced in the silicon feedstock on *p*-type and *n*-type multicrystalline silicon (mc-Si) ingots grown by directional solidification. We investigate its impacts at different stage of the solar cell manufacturing stage with emphasis on the properties of the solar cells in comparison to reference uncontaminated material. The diffusion length is determined directly from spatial resolved as well as average internal quantum efficiencies (IQE) of the solar cells.

We choose to investigate Fe because is a dominant metal impurity in silicon wafers^{2,3}. Typical concentration of total Fe [Fe] in commercial multicrystalline silicon ingots from Neutron Activation Analysis^{4,5} (NAA) measurements has been reported^{2,3} to be about in the range 10^{13} - 10^{15} cm⁻³. It is a relatively fast diffusing impurity ($D = 2.6 \times 10^{-6}$ cm²/s @ 1000 °C)⁶, thus it can be gettered.

It is important to note that the Fe we introduced in the silicon charge is, of course, subject to a similar thermal history and process as would be any Fe present as impurity in the feedstock. The thermal history of the material determines, among other aspects, the fraction of impurities which are electrically active in the Si, the properties of precipitates, etc, and thus the final impact of impurities on the solar cell performance. Our experimental approach differs from previous works (e.g., Ref. 7,8) where Fe was introduced by ion implantation or intentional surface contamination on wafer level, followed by a thermal anneal of the wafer.

Table 1. Ingot descriptions. The dopant and the impurity that have been introduced in the silicon charge.

Label	Crucible	Coating	Dopant (ppm wt)	Impurity (ppm wt)
<i>p</i> -type reference	HP silica	Purified Si ₃ N ₄	B 0.116	-
<i>p</i> -type Fe	HP silica	Purified Si ₃ N ₄	B 0.116	Fe 53
<i>n</i> -type reference	HP silica	Purified Si ₃ N ₄	P 0.318	-
<i>n</i> -type Fe	HP silica	Purified Si ₃ N ₄	P 0.318	Fe 53

We discuss in this article the impact on solar cell performance while a separate article has described the distribution of Fe in the ingots⁹. We believe our studies are

representative and useful for assessment of the impact of unwanted Fe impurities in feedstock and crystallisation materials.

In addition to showing the impact of Fe in multicrystalline cast ingots, this article also shows that the impact of impurities does not only cause a reduction of diffusion length due to interstitial Fe point defects, but also seems to affect the crystallisation process, contributing to a further reduction of the performance of the solar cells.

2. Experimental methods

Four pilot scale ingots have been grown for this study, using a Crystalox DS 250 furnace designed to solidify multicrystalline (mc) ingots by Bridgman-type directional solidification method. This furnace allows growth of 12 kg ingots by the directional solidification method, having a diameter of 250 mm and a height of 110 mm. In order to study the impact of the intentionally introduced contaminant, other sources of contamination (e.g. feedstock, crucible, and coating) have been kept as low as possible. Thus, virgin polysilicon, high purity (HP) crucibles¹⁰ and purified Si₃N₄¹¹ have been used. The dopant and impurity were introduced in the feedstock charge according to Table 1.

The amount of Fe introduced in the melt (53 ppm wt) has been chosen targeting $[\text{Fe}] = 3 \times 10^{13} \text{ cm}^{-3}$ at about three quarters of the ingot height, assuming an effective distribution coefficient equaling the equilibrium coefficient (6×10^{-6})¹.

A full description of the crystallisation process and comprehensive characterisation of the material can be found in Ref. 9. A direct contact between ingot and crucible was observed in some regions of the *p*-type reference ingot. This resulted in interstitial oxygen (O_i) levels of about $4 \times 10^{17} \text{ cm}^{-3}$ in the middle of the ingot, decreasing towards the top. The O_i concentrations in the *p*-type and *n*-type Fe doped ingots are $1.5 \times 10^{17} \text{ cm}^{-3}$ and $3 \times 10^{17} \text{ cm}^{-3}$, respectively, with uniform distribution. The $[\text{O}_i]$ in the *n*-type reference ingot is about $3 \times 10^{17} \text{ cm}^{-3}$.

The *n*-type reference ingot was grown (at an earlier point of time) under different furnace conditions. This resulted in a substitutional carbon concentration of about $7 \times 10^{17} \text{ cm}^{-3}$ in the top of the ingot. This has to be taken into account when interpreting the results from this ingot. The other ingots have a substitutional carbon concentration below $5 \times 10^{17} \text{ cm}^{-3}$.

From each ingot centre a block of $125 \times 125 \text{ mm}^2$ was cut, which was sliced into wafers with a thickness of 240 μm . A set of 10 wafers for each ingot, representative of the complete ingot heights, were processed into solar cells with a baseline *p*-type and *n*-type solar cell process. The *p*-type solar cell process is the state of the art industrial P diffusion Al-Back Surface Field (BSF) SiN_x:H firing through¹². The *n*-type cell process consists of a boron front emitter and phosphorous BSF in a co-diffusion step (B/P co-diffusion), both passivated by SiN_x:H, and firing through metallization with open rear side grid¹³.

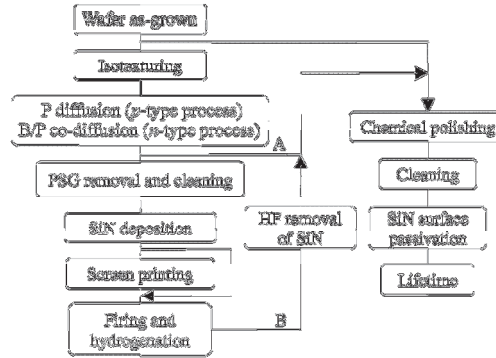


FIG. 1. Solar cell process steps. Wafers are taken out after gettering (A) and hydrogenation (B) to study the impact of each of these steps in comparison to as-grown wafers. The wafers after hydrogenation receive no screen-printing. PhosphoSilicate Glass (PSG).

Neighbouring wafers were used to characterise the minority carrier lifetime after phosphorus (P) diffusion and hydrogenation¹⁴ according to the scheme in FIG. 1. The samples to characterise the P diffusion were removed from the solar cell process after the emitter formation. The emitter was removed by a chemical polishing step (HF/HNO₃), followed by deposition of a SiN surface passivating layer¹⁵ on both sides. The samples to characterise the phosphorous diffusion and hydrogenation were removed from the normal process sequence after SiN_x:H anti-reflection coating (ARC) deposition. They were annealed under the same conditions as for the metallisation firing-through of the regular cells, but without metal applied and with SiN_x:H deposited additionally on the rear side. Subsequently the SiN_x:H ARC was removed with HF. The emitter was etched by a chemical polishing step followed by deposition of SiN surface passivating layers on both sides. An equivalent procedure was performed to prepare lifetime test samples after B/P co-diffusion and hydrogenation, according to the *n*-type cell process. A set of vertically adjacent ('neighbour') wafers were polished and passivated with SiN under the same conditions as the other two sets, to provide the lifetime on as-grown samples.

The surface passivating SiN layers, deposited at low temperature, do not change bulk properties¹⁶ (hydrogen passivation) after deposition and assure a surface recombination velocity less than 50 cm/s, verified by reference float zone (FZ) samples. Thus for high bulk lifetime, the effective minority carrier lifetime, which we report in this article, is an underestimation of the bulk lifetime.

We use the notation "*p*-type Fe" and "*n*-type Fe" to refer to the *p*-type or *n*-type multicrystalline silicon ingot intentionally contaminated with Fe.

3. Results

A. Solar cell characterisation

The bulk doping level is reported in FIG. 2. The lines represent the Scheil distribution¹⁷ of B and P where the equilibrium distribution coefficient for B ($k_{eq}=0.75$

Ref.18,19) and P ($k_{eq}=0.35$ Ref. 18,19) is considered. The bulk resistivity is about $1.0 \Omega \times \text{cm}$ for the *p*-type ingots and ranging from 0.4 - $0.8 \Omega \times \text{cm}$ for the *n*-type ingots.

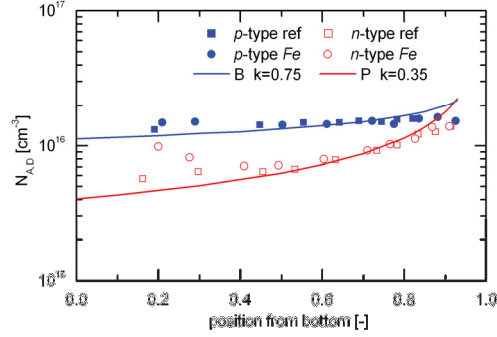


FIG 2. Acceptor and donor concentration for the *n*-type and *p*-type ingots versus vertical position in ingot from bottom (bottom:0, top:1). The lines represent the Scheil distribution of B and P where k denotes the distribution coefficient typically found in literature^{18,19}.

In FIG. 3 the product of the short circuit current (J_{sc}) and the open circuit voltage (V_{oc}) is reported as a function of the vertical position in the ingots. We report the $J_{sc} \times V_{oc}$ product because this value is more representative of the recombination in the solar cells, excluding the variation present in the fill factor (FF) due to process-induced or material-related series resistance and shunts. Only in the bottom and in the top of *p*-type Fe ingot and in the top of the *n*-type reference ingots there is a significant decrease of the FF (shown in FIG. 3). In the *p*-type ingots, three main regions can be distinguished along the ingot height: (i) the bottom half, (ii) the region around 70% height, and (iii) the top of the ingot. In region (ii) the solar cell performances are comparable for the *p*-type Fe and *p*-type reference ingot. In regions (i) and (iii), the bottom half and the top, the cell performances are reduced for the *p*-type Fe ingot compared to the *p*-type reference.

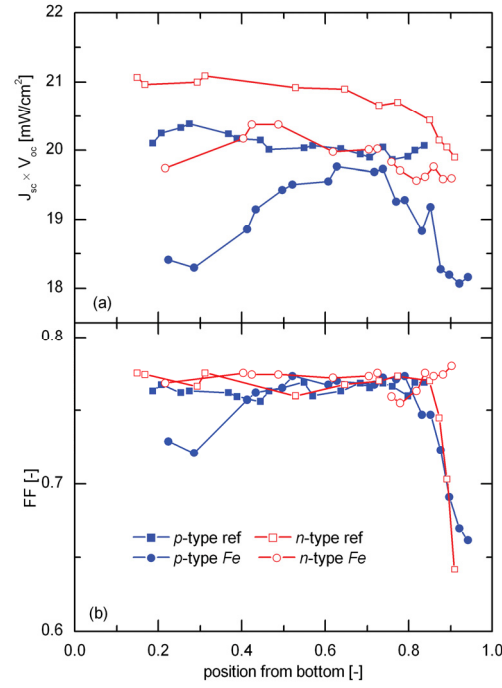


FIG 3. (a): $J_{sc} \times V_{oc}$ and (b): FF versus vertical position in ingot.

In the *n*-type ingots the solar cell performances are reduced in the Fe ingot compared to the reference in the regions (i) and (ii). In region (iii), the top, the performance of the reference ingot decreases and approaches the Fe ingot.

The IQE (FIG. 4) was derived from spectral response and reflectivity measurements for the *p*-type and *n*-type ingots. The IQE curves show that the main differences of the solar cell performance between the reference and Fe doped ingots are in the long wavelength response. The effective average minority carrier diffusion length (L_{eff}) was calculated²⁰ from the curve of $1/IQE$ versus $1/\alpha(\lambda)$, where $\alpha(\lambda)$ is the absorption length in silicon for wavelength λ . The results are reported in FIG. 5. The diffusion length (L_d) is the limiting factor for the solar cell performance.

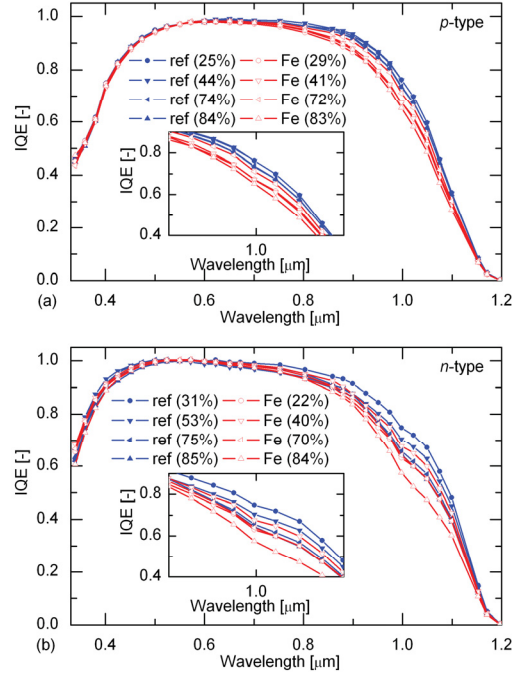


FIG. 4. IQE at different heights in the p-type (a) and n-type (b) ingots.

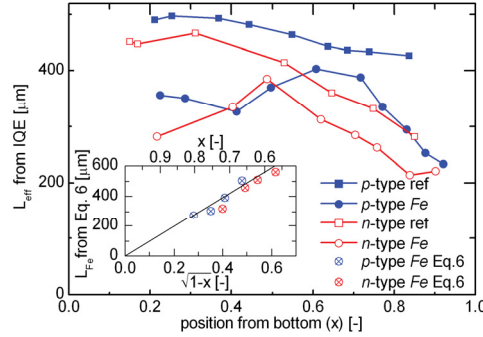


FIG. 5. Diffusion lengths in reference p- and n-type ingots, Fe doped p- and n-type ingots versus vertical position. In the inset, the diffusion length relative to Fe is plotted versus square root of the vertical position from the ingot top.

The spatial distribution of defects has been investigated by maps of local effective diffusion length obtained combining Light Beam Induced Current (LBIC) and reflectance measurements at three different wavelengths over the whole area of the solar cells. These data were converted into maps of internal quantum efficiency and finally to maps of local effective diffusion length²¹, which are shown in FIG. 6. The L_d maps qualitatively represent the grain structure (grains with high defect density give a relatively low LBIC signal and low L_d)²². FIG. 6 shows that there is a difference in the

crystal structure development for the Fe-ingots compared to the reference ingots. At the bottom and top of the Fe-ingots the density of the crystal defects is enhanced, both in comparison to region (ii) in the same ingots, and in comparison to the reference ingots. The histograms of L_d (shown in FIG. 7) will be treated in detail in the discussion section.

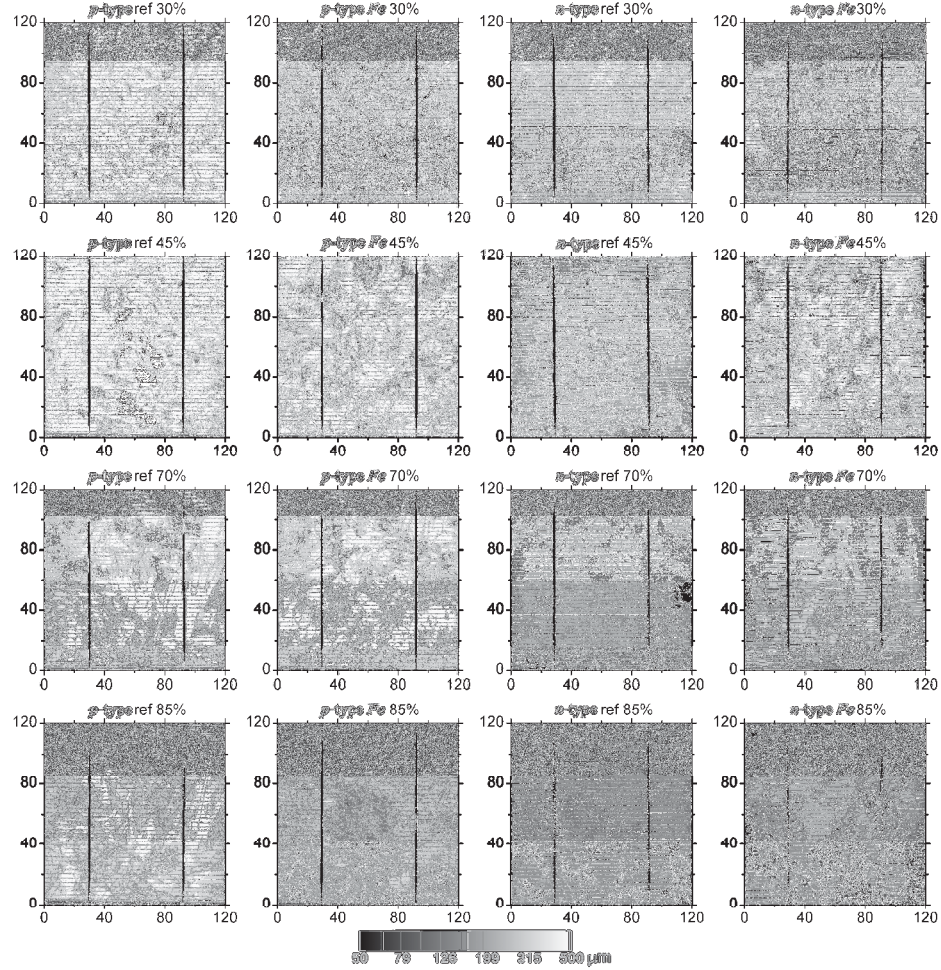


FIG. 6. L_d maps at 30% (upper pictures), 45%, 70% and 85% (lower pictures) of the ingot height respectively. Most left: p-type reference ingot, Centre left: p-type Fe ingot, Centre right: n-type reference ingot, Most right: n-type Fe ingot. The x-y axis values are given in mm.

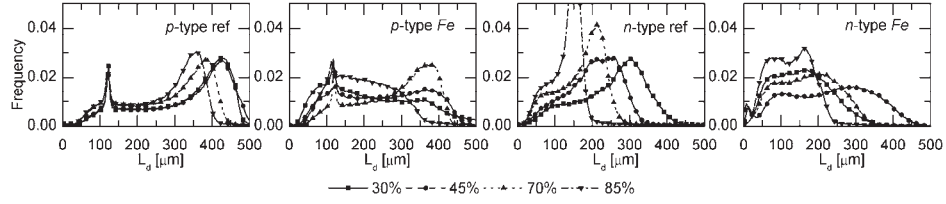


FIG 7. Histograms of L_d maps shown in FIG 6.

B. Minority carrier lifetime changes due to *p*-type and *n*-type solar cell process steps

1. *p*-type solar cell process

The minority carrier lifetime has been measured by Quasi-Steady-State PhotoConductance (QSS-PC) at an injection level of 10^{15} cm^{-3} before and after FeB pairs dissociation^{23,26}. In FIG. 8 the FeB lifetime versus vertical position in the ingot is shown after different *p*-type cell process steps. The *n*-type wafers were processed together with the *p*-type wafers according to FIG. 1. For the *p*-type reference ingot the as-grown lifetime is good and just a minor improvement is seen after gettering and hydrogenation. In the wafers from this ingot, BO-related light induced degradation affected the minority carrier lifetime already after 60s illumination (BO degradation is known to occur in mc-Si wafers^{24,25}). As a result, due to a partial BO-related defect formation during the QSS-PC measurements, the lifetime for the *p*-type reference wafers reported in FIG. 8 is slightly underestimated.

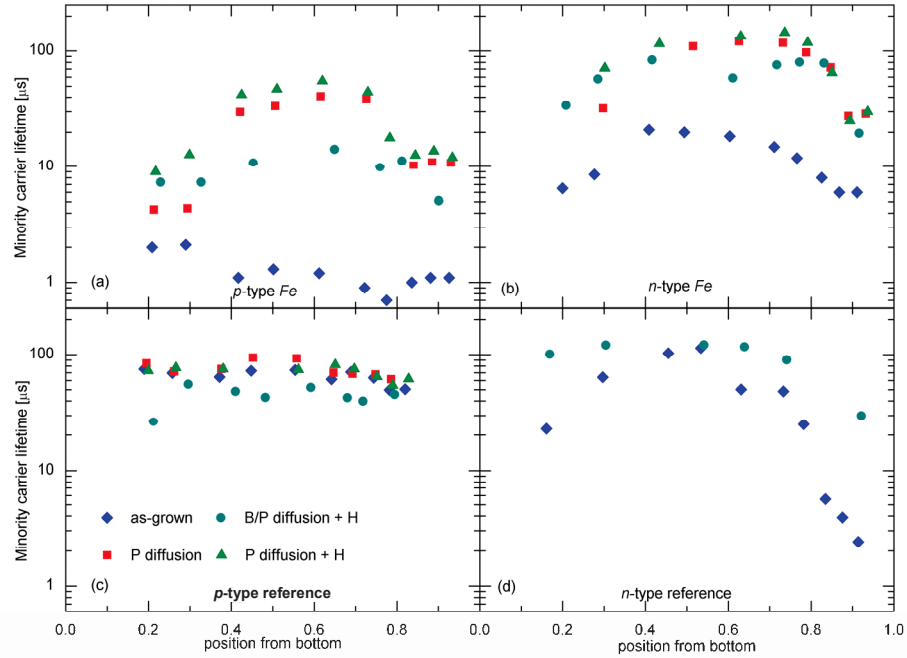


FIG 8. Minority carrier lifetime versus vertical position in the ingots. The data are reported after different solar cell process steps. P diffusion: emitter formation in *p*-type solar cell process. P diffusion + H: emitter formation, $\text{SiN}_x\text{:H}$ deposition and firing as in the *p*-type solar cell process. B/P co-diffusion + H: emitter and BSF formation, $\text{SiN}_x\text{:H}$ deposition and firing as in the *n*-type solar cell process. (a): *p*-type Fe doped. (b): *n*-type Fe doped. (c): *p*-type reference. (d): *n*-type reference.

The as-grown lifetime in *p*- and *n*-type Fe doped wafers is about 1-2 μs and 6-20 μs , respectively. This difference in lifetime between *p*- and *n*-type can be explained by Shockley-Read-Hall (SRH) model applied to interstitial Fe defects, and will be discussed in section IV C. The improvement of lifetime after gettering and hydrogenation of the *p*-type Fe ingot is up to 50 times and of the *n*-type Fe ingot 5 times in the centre of the ingot. After gettering and hydrogenation the lifetimes in the *n*- and *p*-type Fe doped ingots are approaching each other (lifetime is about two times higher in the *n*-type than in the *p*-type ingot). As-grown lifetime values for the *n*-type reference are similar to the gettered values of the *n*-type Fe ingot (FIG. 8).

2. *n*-type solar cell process

In FIG. 8 the lifetime versus vertical position in the ingot is shown after gettering and hydrogenation according to an *n*-type solar cell process. The *p*-type wafers were processed together with the *n*-type in the *n*-type cell process described in section II. The improvements of lifetime after B/P co-diffusion and hydrogenation are up to 10

times and 3-10 times for the *p*-type Fe and *n*-type Fe ingot respectively. The lifetime in the *n*-type Fe ingot is up to 8 times higher than the *p*-type Fe ingot after gettering and hydrogenation.

3. Interstitial iron concentration

In order to quantify the gettering effectiveness by another parameter than lifetime, the interstitial Fe (Fe_i) concentration was derived from lifetime measurements before and after FeB pair dissociation²⁶, only for the *p*-type ingots. In FIG. 9 the interstitial Fe concentration is shown versus vertical position in the *p*-type Fe ingot. The as-grown $[Fe_i]$ is about 10^{13} cm^{-3} in the middle of the ingot and decreases to about 10^{11} cm^{-3} after phosphorous diffusion. After subsequent hydrogenation active $[Fe_i]$ is further reduced by a factor two. The concentration of Fe_i after B/P co-diffusion and hydrogenation is about 10^{12} cm^{-3} . The $[Fe_i]$ of as-grown wafers are indicative since the lifetime of these wafers is very low (1-2 μs), which reduces the measurement accuracy ($[Fe_i]$ is derived from a very small change in lifetime, and dissociation is more difficult to accomplish).

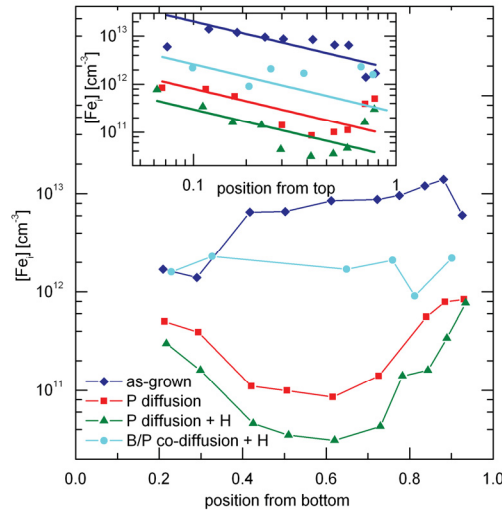


FIG 9. Interstitial Fe concentration versus vertical position in *p*-type Fe doped ingot. The data are reported after different solar cell process steps. The $[Fe_i]$ was derived from lifetime measurements before and after FeB dissociation. In the inset the $[Fe_i]$ is reported versus vertical position from the top. The lines in the inset are Scheil equation fits (Eq. 3) to the measured data, with $k < 0.01$ (for all $k < 0.01$ the slope of the curves does not noticeably depend on k anymore).

4. Discussion

In this section the results are discussed separately by topic. In the first paragraph (Section IV A) the reduced performance of the solar cells are analysed discussing the different contributions to the diffusion length reduction. The following paragraph

investigates the spatial distribution of crystal defects and shows interaction with the contamination of Fe. At last the minority carrier lifetime and interstitial Fe concentration at different stage of the solar cell process are discussed in Section IV C.

A. Solar cells

The addition of 53 ppm wt Fe to the feedstock causes an overall lowering of solar cell performance compared to the reference. The performance is, however, remarkably close to the reference at positions between about 60 and 70% of the ingot height for the *p*-type ingots. In the *n*-type ingot, the addition of Fe reduces the solar cell performance in most of the ingot. The main reason for the degradation is a reduction of the diffusion length (FIG. 5).

In the *n*-type ingots, the Fe contamination results in a decrease of V_{oc} which could not be fully explained by a lower diffusion length in the base, in 1-dimensional cell modelling (using PC-1D²⁷). The V_{oc} decrease may be related either to the contamination of the emitter or to the spatial inhomogeneity in the bulk properties. However, an increase of recombination in the emitter region is not visible in the IQE measurements at short wavelengths (FIG. 4) differently than reported by Macdonald²⁸. Further experimental work is needed in order to discriminate between the possible causes.

In the *n*-type reference, the significant decrease of the FF in top can be related to the high substitutional carbon concentration found in the top region (see section II). The impact of carbon on the solar cell performance is not completely known²⁹, however, SiC precipitates are known to cause shunt in the solar cell^{30,31,32}.

In order to analyse the different contributions to the reduction of the diffusion length, we compare L_d with the expected trend for a metal impurity concentration in the ingot. The equation describing the diffusion length as a function of lifetime (τ) is

$$L_d = \sqrt{D\tau}, \quad (1)$$

the lifetime as a function of point defect density (N_t) is

$$\tau \propto \frac{1}{N_t} \quad (2)$$

and the Scheil equation describing the segregation of impurities is

$$N_t = \beta C_s = \beta k C_0 (1 - x)^{(k-1)} \quad (3)$$

where C_s is the total impurity concentration, k is the distribution coefficient and x is the fractional ingot height from bottom ($0 \leq x \leq 1$). β is the percentage of total impurity which is electrically active as point defect. Combining Eq. 1, 2 and 3 gives the following relation to be expected for diffusion length as a function of position in ingots dominated by metal point defects and assuming $k \ll 1$.

$$L_d \propto \sqrt{1-x} \quad (4)$$

The diffusion length in the *p*-type reference is relatively flat (see FIG. 5) where only a slight decrease of diffusion length towards the top of the ingot is observed. This could mean that the transition metals distribution effect (eq. 3) is small compared to other causes for reduction of lifetime, such as recombination at crystal defects (e.g. dislocations and grain boundaries).

In order to isolate the impact of Fe, the total recombination in the Fe ingots ($1/\tau_{\text{eff}}$) can be approximated as the impact of added Fe ($1/\tau_{\text{Fe}}$) plus the impact of crystal defects ($1/\tau_{\text{crystal-defect}}$)

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{Fe}}} + \frac{1}{\tau_{\text{crystal-defect}}} \quad (5)$$

We use the reference ingot to estimate $\tau_{\text{crystal-defect}}$. Indeed this assumes that the impact of the added Fe does not change the recombination due to the crystal structure. We will see later that this assumption may not be valid in parts of the ingot. Using Eq. 1 gives then

$$\frac{1}{L_{\text{Fe}}^2} = \frac{1}{L_{\text{eff}}^2} - \frac{1}{L_{\text{Ref}}^2} \quad (6)$$

The Fe dependent diffusion length (L_{Fe}) versus $\sqrt{1-x}$ is included in the inset of FIG. 5. This diffusion length, in both Fe ingots, shows a linear trend with $\sqrt{1-x}$ in the top half of the ingots. This means that L_d is limited by a mechanism which is governed by the Scheil equation, such as the segregation of Fe in the solid silicon. The interpretation of this result is discussed, together with the distribution of $[\text{Fe}_i]$, at the end of Section IV C. Clearly, the calculation of L_{Fe} using Eq. 6 becomes inaccurate when L_{eff} and L_{Ref} are close.

B. Crystal structure

The L_d maps (see FIG. 6) show grain structures which are significantly different in the Fe ingots compared to the references, and with a significant change occurring within the Fe ingots themselves. In order to study this structure we discriminate between low and high recombination areas. High recombination areas correspond qualitatively to grain boundaries (GBs) and dislocations, and quantitatively to areas with L_d around 100 μm in the histograms of FIG. 7. Low recombination areas correspond to the intragrain regions (L_d around 400 μm in the histograms of FIG. 7).

In the *n*-type ingots, both the reference and Fe doped ingot, there is a reduction of L_d in the intragrain areas going from the bottom to the top of the ingots. The same behaviour is present, but much less evident, in the *p*-type reference ingot. The most harmful impurities in *n*-type wafers are mainly substitutional³³ and thus have a low diffusivity. The higher evidence of impurity segregation in *n*-type cells may be related

to less effective gettering due to this low diffusivity of "important" impurities, as well as due to the B/P co-diffusion taking place at higher temperature in the cell process.

In the bottom and at the top of both Fe ingots, there are more low L_d areas, which correspond to GBs and dislocations. This is evident from the histograms (see FIG. 7). The area of low L_d decreases from the bottom to the centre and then increases again towards the top. Both the reference ingots have lower low L_d areas and comparable crystal structure from bottom to top.

The L_d distribution (FIG. 7) at about 70% height of the p -type Fe ingot is comparable to that of the p -type reference. Note that the solar cell performances are comparable as well at this height.

The addition of Fe in the p - and n -type ingots causes a decrease of the diffusion length in top of the ingots due to segregation and increase of dissolved metal impurities. Our results indicate that this is, however, not the only effect of the high levels of Fe. The increased crystal defect concentration in the top and bottom of the ingots (represented by the low- L_d peaks in the histograms in Fig. 7) contributes considerably to solar cell performance degradation. We believe these are also related to the Fe contamination. The increasing defect concentration in the top of the ingots may be related to the increasing iron concentration in the melt (due to the segregation), that affects the growth process. A known example of the impact of impurity concentration on the crystal growth is the constitutional supercooling, as observed earlier on intentionally contaminated ingots^{34,35}. In our case, however, the effect is not as severe as constitutional supercooling. In the bottom of the ingot, the high concentration of Fe in the silicon melt may have initiated or enhanced a disturbance of nucleation and growth during the early solidification phase. Although it is known from practice that the initial phase of ingot growth is susceptible to disturbances, literature on this phenomenon is scarce. Verification of the hypothesis that the increased crystal defect density in the bottom of the Fe doped ingots is related to the high Fe concentration would require additional dedicated experiments and modelling.

C. Minority carrier lifetime

In this paragraph we consider the impact of the Fe introduced in p - and n -type ingots on the lifetime at different stage of the solar cell process. The interstitial iron variations are discussed in the last paragraph.

Table 2. Minority carrier lifetime improvements compared to as-grown after diffusion and hydrogenation in the centre of the ingot.

Process	p -type Fe wafers	n -type Fe wafers
P diffusion + Hydrogenation	~50x	~5x
B/P co-diffusion + Hydrogenation	~10x	~4x

The interstitial Fe capture cross section for electrons is nearly three orders of magnitude higher than for holes³⁶. However, the as-grown lifetime in *n*-type Fe ingot is only one order of magnitude higher than in the *p*-type (see FIG. 8) at an injection level of 10^{15} cm^{-3} . This is much less than the Fe capture cross section ratio for electrons and holes. However, taking in consideration the injection level at which the lifetime has been measured and the Fe concentration, the SRH curves appropriate for the *p*-type wafers already significantly bend upwards (see FIG. 10). At 10^{15} cm^{-3} the lifetime in the *p*- and *n*-type differ by a factor ten in agreement with experimental data. The difference between *n*-type and *p*-type lifetime in the Fe doped ingots can be explained by the physical properties of iron. In order to predict the effect of Fe in *p*- and *n*-type cells, it is important to know the injection level at the solar cell working condition. After gettering, the amount of Fe is reduced and so is the overall recombination. Therefore the injection level increases and the gap between *n*-type and *p*-type SRH lifetime curves decreases. In particular the emitter recombination current and the Auger recombination³⁷ become dominant and the lifetime is similar as shown in FIG 11. However, in case other recombination mechanisms are present, the injection level is lower and the gap *n*-/*p*-type increases. After diffusion and hydrogenation the lifetime of both *p*-type and *n*-type Fe doped ingots increase. In Table 2. the lifetime improvement after diffusion and hydrogenation of *p*-type and *n*-type cell process is summarised. The most harmful impurities in *n*-type wafers are mainly substitutional. The reduced gettering effectiveness of the *p*-type cell process (i.e., the phosphorus diffusion), in *n*-type wafers compared to *p*-type wafers might be explained by the presence of non-getterable defects, such as substitutional impurities. However the surface passivation might also limit the lifetime in the *n*-type wafers (see section II). The lifetime improvement on *p*-type wafers is reduced with the B/P co-diffusion compared to the phosphorous diffusion. The gettering by boron diffusion is less effective than the phosphorous diffusion²⁸. In addition B/P co-diffusion takes place at a higher temperature which is not the optimal temperature for gettering^{38,39} and a larger amount of impurities can dissolve from precipitates and diffuse.

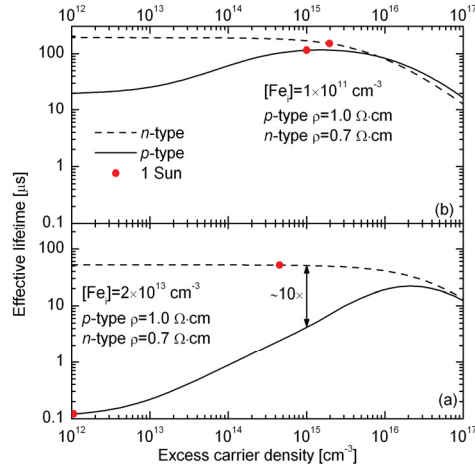


FIG. 10. Injection level dependent lifetime in *p*-type and *n*-type due to Fe_i . (a): $[Fe_i] = 2 \times 10^{13} \text{ cm}^{-3}$ as measured in as-grown *p*-type wafers. (b): $[Fe_i] = 1 \times 10^{11} \text{ cm}^{-3}$ as measured after *P* diffusion and hydrogenation in *p*-type wafers. An emitter recombination current (J_{0e}) of $1 \times 10^{-13} \text{ A/cm}^2$ has been used. The band to band and Auger recombination were considered³⁷.

1. Lifetime in the *p*-type versus *n*-type solar cell process

The lifetime maps can give more insight in the local variation of recombination centers, in these experiments and particularly for Fe.

The lifetime spatial distribution after several solar cell process steps has been investigated by means of Modulated Free Carrier Absorption⁴⁰ (MFCA) technique. In FIG. 11 the lifetime maps of neighbouring wafers from the middle of the *p*-type *Fe* ingot are shown after each solar cell process step (as-grown, after diffusion and after hydrogenation). The as-grown samples have been measured with a bias light intensity of 25 suns, also to avoid minority carrier trapping artefact, and the samples after phosphorous diffusion and hydrogenation with 2.5 suns. The as-grown lifetime map shows several GBs rimmed, along their length, by higher lifetime boundaries. QSS-PC lifetime measurement shows that most of the traps are filled at 25 suns illumination. The higher lifetime reported is not due to trapping. GBs can act as sink for impurities (also known as internal gettering^{35,41,42}), which cause an impurity depletion region beside the GBs. It should be noted that higher lifetime is visible close to GBs while intragrain areas have the lowest lifetime.

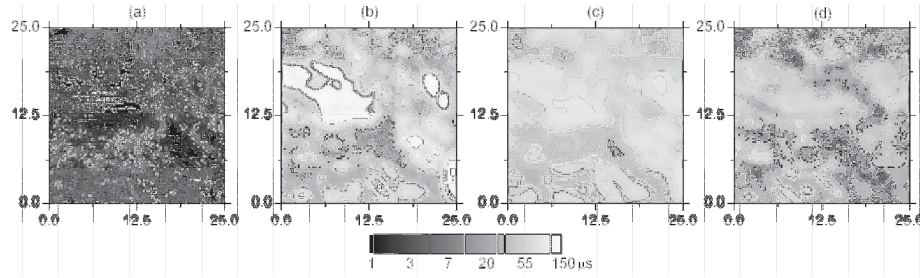


FIG. 11 Lifetime map as measured by Modulated Free Carrier Absorption⁴⁰ on neighbouring wafers at ~75% height of the p-type Fe ingot. The resolution used is 250 μm . The as-grown sample (a) has been illuminated with a bias light of 25 suns. Most of the traps are filled at this corresponding injection level as determined by QSS-PC measurements. The samples after P diffusion (b), P diffusion + hydrogenation (c) and B/P co-diffusion + hydrogenation (d), have been illuminated with a bias light of 2.5 suns.

The maps show that the lifetime increases extremely after phosphorous diffusion especially in the intragrain areas. After hydrogenation the darker areas improve, showing the passivation of defect areas (GBs and areas with high dislocation density)^{43,44,45}. On the other hand, in the higher lifetime areas, which correspond to intragrain areas, the lifetimes slightly decrease. The degradation of intragrain areas after hydrogenation is observable also in different material in an earlier work¹⁴ but not discussed. In this areas, the high lifetime ($>100 \mu\text{s}$) can also be limited by the surfaces recombination. The overall impact of hydrogenation is visible in the histogram of FIG. 12, where the lifetime distribution is reduced at high lifetime after hydrogenation. On the other hand, the low lifetime distribution improves. The $1/\tau$ averaged⁴⁶ lifetime increases from 47 μs to 58 μs after hydrogenation, confirming the beneficial effect of the hydrogenation. As a reference, the as-grown $1/\tau$ averaged lifetime is 2.4 μs .

The lifetime distribution after B/P co-diffusion and hydrogenation has the same shape of the distribution after phosphorous diffusion and hydrogenation but the entire curve is shifted towards low lifetime for the B/P co-diffusion. The lifetime map of this sample looks less homogeneous and several crystal defects, hardly visible in the phosphorous diffusion wafer, are still active. The passivation of GBs, and crystal defects in general, depends on the GBs character⁴⁷ and impurity level. Since the samples are neighbouring, the GBs character and as-grown impurity distribution and precipitates are similar. The activity of the crystal defects is, therefore, due to the higher impurity level after the B/P co-diffusion compared to the phosphorous diffusion.

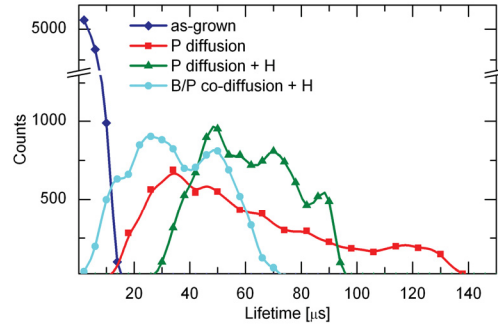


FIG. 12 Lifetime distribution after different solar cell process step.

2. Interstitial iron concentration

From Eq. 3 and by knowing the $[Fe_i]$ in the as-grown wafers it is possible to calculate the percentage of total Fe which is electrically active (β) after the ingot crystallisation. We fit the experimental data in FIG. 9 considering the initial Fe concentration (C_0) in the silicon melt (the Fe introduced, 53 ppm wt), the effective distribution coefficient of 2×10^{-5} for Fe in the *p*-type Fe ingot determined by means of NAA and Glow-Discharge Mass Spectroscopy analyses in Ref. 9, and β as a fit parameter. As a result $\beta = 0.1$, i.e., the Fe_i concentration is about 10% of the total concentration of Fe.

The active $[Fe_i]$ after hydrogenation is reduced by a factor of two in the *p*-type Fe ingot, as shown in FIG. 9. An earlier study has shown the passivation of Fe by means of hydrogen⁴⁸. The determination of $[Fe_i]$ by means of lifetime measurements is, however, affected by lifetime inhomogeneity. This results in an overestimation of the $[Fe_i]$ depending on the level of inhomogeneity²³, as in the sample after gettering (FIG. 11 b). An estimation of the magnitude of this effect is not trivial. As an example, a lifetime inhomogeneity of 50% (50% of the total area has good lifetime and 50% bad lifetime) can cause an overestimation in the $[Fe_i]$ by a factor of two.

The concentration of $[Fe_i]$ after hydrogenation is lower by more than one order of magnitude in the phosphorous diffused wafer than in the B/P co-diffused wafers (see FIG. 9), confirming the reduced Fe gettering by the B/P co-diffusion process.

The inset of FIG. 9 shows the interstitial Fe concentration after different process steps versus position from top for the *p*-type Fe ingot. The lines in the inset (FIG. 9) are an attempt to fit the Scheil equation (Eq. 3) to the measured data, using $k < 0.01$ (for all $k < 0.01$ the slope of the curves does not noticeably depend on k anymore). The data at the top (>90%) and at the bottom (<20%) are affected by solid-state impurity diffusion during the ingot cooling and by the presence of highly dislocated areas which are known to affect the gettering effectiveness^{49,50}.

The concentration of interstitial Fe after phosphorous diffusion, and after diffusion and hydrogenation, is not constant but shows a trend roughly referable to the Scheil equation. This is an interesting and perhaps somewhat surprising result, which is

visible on wafer level (lifetime and $[Fe_i]$ after diffusion and diffusion + hydrogenation) as well as on solar cell level (diffusion length calculated in Section IV A). The cause of this trend is uncertain. Impurity gettering is a complex process governed by impurity diffusion to the gettering layer, dissolution of precipitates, and reprecipitation. If the precipitates are not completely dissolved and the sample is cooled fast enough, the concentration of Fe_i should be equal to the solubility of Fe at the gettering temperature³⁹. In a simple approximation, the $[Fe_i]$ after gettering should thus be independent of the wafer position since the gettering is done under the same conditions (thermal profile) for all the wafers. However during the cool down, Fe_i can still diffuse, be gettered, or reprecipitate. Indeed the observed $[Fe_i] \sim 10^{11} \text{ cm}^{-3}$ is lower than the solubility of Fe at the gettering temperature. A more correct description should include the impact of the crystal structure. Towards the top of the ingot the crystal structure gets worse (see FIG.6). Since the gettering effectiveness is known to depend on the crystal structure, this might explain the observed trend for $[Fe_i]$. A detailed interpretation of these results is outside the purpose of this paper and requires modelling of precipitate dissolution involving their size and density. To our knowledge a comparison of impurity concentrations with segregation curves after gettering has not been reported before.

5. Conclusions

53 ppm wt of Fe has been introduced in the silicon feedstock before the melting and the subsequent solidification of a *p*-type and an *n*-type doped ingot. The differences in the as-grown lifetime between *p*- (1-2 μs) and *n*-type (6-20 μs) Fe doped Si ingots are explained with SRH theory for interstitial Fe defects. We observe that some GBs act as sink for impurities, causing a cleaner, higher lifetime region beside these GBs. The as-grown $[Fe_i]$ in the *p*-type Fe doped ingot is in the order of 10^{13} cm^{-3} , which represent about 10% of the total iron concentration.

p-type and *n*-type solar cell processes were applied both to wafers sliced from the Fe doped ingots and reference ingots produced from non-Fe doped silicon feedstock. After phosphorous diffusion and hydrogenation, the improvement of lifetime is up to 50 times for the *p*-type Fe doped ingot and 5 times for the *n*-type Fe doped ingot. After boron/phosphorus co-diffusion and hydrogenation the improvement is about 10 times for the *p*-type ingot and about 4 times for the *n*-type ingot. The $[Fe_i]$ drops from about 10^{13} cm^{-3} to about 10^{11} cm^{-3} in the *p*-type Fe ingot after phosphorous diffusion. The concentration of Fe_i after B/P co-diffusion and hydrogenation is about 10^{12} cm^{-3} , which confirms the reduced Fe gettering of the B/P co-diffusion process.

The concentration of interstitial Fe after the solar cell processing (P diffusion and hydrogenation) shows a trend along the ingot which roughly follows the Scheil equation. A decrease of the solar cell diffusion length, which can be ascribed to a Scheil-like distribution of active Fe is observed as well.

Passivation of GBs and areas with high dislocation density by means of hydrogenation is observed.

There is a difference in the crystal structure development for both the Fe doped ingots compared to the reference ingots. At the bottom and at the top of the Fe doped ingots the density of the crystal defects is enhanced, both in comparison to

about 70% height within the same ingots, and in comparison to the reference ingots. This is reflected in the solar cell efficiencies, which are reduced in the bottom and top, but are comparable to the reference at around 70% height.

The increasing defect concentration in the top of the Fe doped ingots may be related to the increasing iron concentration in the melt. In the bottom, the initial high concentration of Fe in the silicon melt may have originated a transient nucleation and growth disturbance during the early solidification phase.

Acknowledgements

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Solar grade silicon feedstock specifications

and conclusions

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 '70s^[1], which represent the early phase of the terrestrial use of photovoltaics (PV) following the oil crisis. It is meant to define the particular quality ("grade") of feedstock suitable for the photovoltaic industry, as distinguished from Electronic Grade (EG) feedstock suitable for the microelectronics 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"^[2] 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 entitled "Arriving to SoG silicon feedstock specifications" was organized in Amsterdam.

The most relevant aspect of a SoG feedstock, which resulted from the workshop discussion in Amsterdam, 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), a.k.a. Upgraded Metallurgical Grade (UMG) or Direct Route feedstock Purification (DRP)). Compensation of P and B during the crystallization on one side and feedstock blending on the other are the most immediate ways to deal with dopants. However, this approach has limitations due to yield and resistivity issues (see [3]). 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 5.1).

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 as that obtained using electronic grade purity feedstock^[4,5,6]. The 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.

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 5.1. 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^[7,8], 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%⁹. 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 electronic-grade silicon, overstating the requirements suitable for the vast majority of anticipated production. Moreover, there are developments in cell architectures with a reduced sensitivity to material quality, which may broaden the application areas of lower grades of silicon even further.

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 (a.k.a. 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 non-metal 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 non-metal 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 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 percent). 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 Ωcm in combination with the 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 Czochralski (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 shift the last stage of feedstock purification to the wafer and cell fabrication processes.

By opening the process tolerance window for silicon feedstocks, 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.

Table 5.1 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*		<0.008	
K*		<0.014	
Zn	-	<2	-
Ca	-	-	-
C	<5	<1 (Cz); <30 (DSS)	
O	<5	<20	-
N	-	-	-

*To avoid crucible devitrification (very conservative);

The general thought behind the categories proposed at the CrystalClear workshop is that they allow to correlate 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 approach to the specifications is 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 which do not fit exactly within predetermined categories. Also technology categories such as UMG, where feedstock characteristics may vary substantially from producer to producer, will be penalised. Many purification methods fall within this category, however, the content of dominant impurities and the overall feedstock purity differ considerably. The advantage of this approach is that it is relatively straightforward, but, on the other hand, its usefulness for solar cell manufactures is limited, since the direct relation with cell performance is lost.

The "CrystalClear" workshop on "SoG silicon feedstock specifications" gave also input to start an initiative ^[10] for the industrial standardization of silicon feedstock specifications via the institution of the Silicon Feedstock Task Force ^[11] by SEMI ^[12].

Another initiative to mention is the Chinese standardisation process for polysilicon under AQSIIQ^[13]. 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 the relevant parameters needed to be specified and, at the same time, to define measurement methods and sampling procedures which should be employed. This is the direction that the standardisation initiative^[11] by SEMI is heading to.

A detailed description of analytical techniques for impurities in silicon feedstock is reported in [14], together with updated references which can be found in [15]. Information on detection limits in silicon can be found in [15,16].

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, in case 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 Chapter 4 of this thesis and the references therein 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.

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Summary

Introduction

Direct conversion of solar energy into electricity by solar cells is a rapidly growing technology. More than 80% of global solar cell production is currently based on silicon. In the past three decades silicon PhotoVoltaic (PV) modules have experienced an average price reduction of 20% for every doubling of the accumulated sales. The availability of silicon of (assumed) sufficient chemical purity ($>7\text{ N}$), however, has been an important limiting factor for rapid growth and price reduction during part of the past decade, and may become one again in the future. The very high cost of investment for conventional poly-Si production plants is a barrier to solve this bottleneck, and becomes even more problematic in times of financial crisis. Furthermore, alternative production processes with lower energy consumption and hence, shorter energy-payback times and smaller carbon footprints based on the corresponding silicon become more important as overall sustainability of energy technologies is set as a development target. Therefore, there is a strong need for low-cost and low-investment-cost technologies for the production of silicon for PV applications. However, such low-cost production technologies will most likely compromise the purity of the resultant silicon. The aim of the studies presented in this thesis is to understand the complex relation between the impurity content of the silicon starting material (the “feedstock”) and the resulting solar cell device performance, taking into account the effects of processing and device architecture.

Impurities in silicon: sources and mitigation of their effect on solar cell performance (Chapter 1)

Impurities are introduced and removed during most of the steps of the PhotoVoltaic (PV) module production chain. It is important to note that quartz, used as the source of silicon in feedstock production, is not the only source of impurities. Important additional sources of impurities are, in fact, the carbon-based reducing agents used for the carbothermic production of silicon (coal, coke, charcoal or woodchips), which contain calcium, phosphorous, sulfur, and also metallic impurities in different amounts. The electrodes and the construction materials of the furnaces themselves introduce iron, chromium, nickel as well as other metals. 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 (Cz) and Directional Solidification (DS) furnaces, and consumables which are in direct contact with the silicon, such as quartz crucibles or SiN lining, are responsible for additional contamination.

Segregation during crystallisation considerably reduces the concentration of transition metals. Impurity gettering and defect passivation take place during emitter formation and $\text{SiN}_x\text{:H}$ deposition and contact formation. Impurity gettering is a kind of solid/solid segregation process, caused by the higher solubility of impurities in (for instance) the phosphorous rich layer (used as emitter in p-type wafers), which removes impurities from the wafer bulk. Fast and relatively fast diffusing impurities such as Fe, Cr, Cu and Ni can be gettered in this way. Passivation of defects (purely crystallographic or impurity-related) may take place upon introduction of hydrogen into the silicon during specific cell processing steps, for instance during the metal contact formation, when hydrogen diffuses from the H-rich SiN_x antireflection layer into the silicon wafer.

Segregation of impurities (Chapter 2)

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

Role of impurities in crystalline silicon (Chapter 3)

The solar cell conversion efficiency is directly related to the cell's ability to collect (separate) the electron-hole pairs formed by incident photons. Charge carriers recombining before they are collected do not contribute to the current output of the device. Carrier recombination also influences the device output voltage. Recombination therefore determines the solar cell power output to a large extent. Deep levels in the silicon band gap, caused by defects and impurities, increase this recombination and thus reduce power output (and hence, cell efficiency). 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 very difficult to tackle, being insensitive to any gettering process. Fast or relatively fast impurities like Cu and Fe are not as harmful even at relative high concentrations 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 as well is strongly reduced, since in that case they remain in the defect-recombination-sensitive part of the solar cells (i.e. the silicon bulk). The Shockley Read Hall (SRH) model allows to predict the impact of the impurities on the lifetime, once the recombination parameters and defect concentrations are known. However, to predict the impact of impurities on the solar cell performance, the amount of electrically active impurities (contributing

to the defect or trap density N_t) needs to be known (besides the impurity recombination parameters), as well as the precipitates size and distribution together with operational injection level of the solar cell. This is quite ambitious and dedicated investigations which relate the initial impurity in the feedstock to the final solar cell efficiency need to be carried out.

Impact of metal impurities on solar cell performance (Chapter 4)

The paramount work carried out in the '70s and '80s 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 which relates the concentration of impurities in silicon wafers, estimated from the effective segregation coefficient, with the solar cell efficiency. However, because of numerous improvements in cell processes since then, the increased use of DS 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.

Recently the author revisited the Westinghouse work, carrying out a systematic study on intentionally contaminated polysilicon and its effect on the solar cell performance within the European Integrated project *CrystalClear* and the European project *Foxy*. Among the most important differences are the facts that the data refers to a modern, state of the art industrial screen-print solar cell process, and that the impact of impurities is investigated on DS multicrystalline ingots and Float-Zone (FZ) ingots, as opposed to Cz silicon ingots. In this updated work the direct relationship between impurities in the feedstock and the final solar cell performance is reported and analyzed. This provides the most straightforward and meaningful interpretation, especially addressed at specifying the feedstock impurity tolerances. The conclusions, therefore, do not rely on impurity analysis or estimated segregation coefficients.

Impact of Fe and Mo in FZ silicon solar cells (Chapter 4.1)

In this work we study the role of iron and molybdenum when intentionally introduced in the feeding rods for the crystallisation of FZ ingots. FZ ingots can be grown from mono- or multicrystalline seeds, resulting in mono- or multicrystalline ingots. This permits to study the incorporation and impact of impurities when present together with grain boundaries (GBs). Carrier lifetime maps on monocrystalline wafers show a uniform lifetime which decreases with the increase of Fe and Mo contamination levels. Multicrystalline wafers show low lifetime areas, corresponding to GBs and highly dislocated areas, which are independent of the contamination levels. On the other hand, intra-grain areas have higher lifetimes, which change with the contamination levels. Uncontaminated multicrystalline cells show a reduced carrier diffusion length compared to the uncontaminated

monocrystalline cells, as a results of GB and dislocation recombination activities. In multicrystalline cells the lowest level of Fe introduced (10^{12} at/cm³) has hardly any influence, whereas in the Mo-contaminated cells the impact is visible already at the lowest level introduced (10^{11} at/cm³). In monocrystalline cells the diffusion length is reduced already at the lowest contamination level of Fe. However this does not have a big effect on cell performance because the diffusion length is still long enough to allow carrier collection.

Impact of Fe, Cr, Ni, Ti and Cu in multicrystalline silicon solar cells (Chapter 4.2)

The impact of impurities on solar cell performance has been investigated. The transition metals iron, chromium, nickel, titanium and copper have been considered in this study. Each impurity has been intentionally added to the silicon feedstock used to grow p-type DS multicrystalline silicon ingots. The contamination levels are chosen targeting typical levels of such impurities in silicon ingots while aiming for a noticeable effect on both wafer and cell level in comparison to uncontaminated reference material. A state-of-the-art screen-print solar cell process has been applied to wafers cut from the ingot from the bottom to the top. The obtained solar cells have been characterized and compared to reference uncontaminated solar cells to correlate the cell performance with the impurity contamination levels. Adding 50 ppm by weight (wt) of iron or 40 ppm wt of nickel or chromium to the silicon feedstock results in solar cell performances similar to the reference values in the position range of 40 to 70% of the ingot height. Addition of 10 ppm wt of titanium dramatically reduces the efficiency along the entire ingot. Impurities like iron, chromium and titanium cause a reduction of the carrier diffusion length in the wafer. Nickel does not have an impact on the diffusion length even at the highest concentration added to the feedstock (200 ppm wt). On the other hand nickel strongly affects the emitter recombination, thereby also significantly reducing the solar cell performance. Copper has the peculiarity to impact both the bulk recombination and the emitter recombination.

Two models have been derived to fit the degradation along the entire ingot based on the Scheil distribution of impurities. The solar cell performance has been modeled as a function of the base bulk recombination and the emitter recombination. The models fit the experimental data very well and have also been successfully validated using ingots with different concentration levels of impurities. Unexpectedly, the Scheil distribution of impurities along the ingot leaves its fingerprint also at the end of the solar cell process.

This model has been used to classify the harmfulness of each impurity and to estimate the impact of a certain amount of impurities in the feedstock on the solar cell performance. A measure of impurity impact has been defined as the level of impurity which causes a relative performance degradation of about 2%_{rel} up to 90% of the ingot height. This directly relates the added concentration of impurities to the solar cell performance and it is not dependent on knowledge of the effective segregation coefficients, the capture cross sections and the electrical activities individually, since only their product is the fitting parameter used in the model. The

result is that 8 ppm wt of Cr, 11 ppm wt of Fe, 0.1 ppm wt of Ti, 4 ppm wt of Ni and 8 ppm wt of Cu are all equivalent in terms of solar cell performance (degradation). The advantage of this parameter is that it includes all the different physical properties of a specific impurity in one single parameter which can be easily compared.

Impact of Fe in p-type and n-type multicrystalline silicon solar cells (Chapter 4.3)

About 50 ppm wt of Fe has been introduced in the silicon feedstock before the melting and the subsequent solidification of p-type and n-type doped ingots. The differences in the as-grown carrier lifetimes between p- (1-2 μ s) and n-type (6-20 μ s) Fe contaminated Si ingots are explained with SRH theory for interstitial Fe defects. We observe that some GBs act as sink for impurities, causing a cleaner, higher lifetime region beside these GBs. The interstitial defect concentration in as-grown material $[Fe_i]$ in the p-type Fe doped ingot is in the order of 10^{13} at/cm³, which represent about 10% of the total iron concentration. p-type and n-type solar cell processes were applied both to wafers sliced from the Fe doped ingots and from reference ingots produced from non Fe doped silicon feedstock. After phosphorous diffusion and hydrogenation, the improvement of carrier lifetime is up to 50 times for the p-type Fe doped ingot and 5 times for the n-type Fe doped ingot. After boron/phosphorus co-diffusion and hydrogenation the improvement is about 10 times for the p-type ingot and about 4 times for the n-type ingot. The $[Fe_i]$ drops from about 10^{13} at/cm³ to about 10^{11} at/cm³ in the p-type Fe ingot after phosphorous diffusion. The concentration of Fe_i after B/P co-diffusion and hydrogenation is about 10^{12} at/cm³, which confirms the reduced Fe gettering of the B/P co-diffusion process.

The concentration of interstitial Fe after the solar cell processing (P diffusion and hydrogenation) shows a trend along the ingot which roughly follows the Scheil equation. A decrease of the solar cell diffusion length, which can be ascribed to a Scheil-like distribution of active Fe is observed as well.

Passivation of GBs and areas with high dislocation densities by means of hydrogenation is observed.

There is a difference in the crystal structure development during crystallization for both Fe doped ingots compared to the reference ingots. At the bottom and at the top of the Fe doped ingots the density of crystal defects is enhanced, both in comparison to about 70% of the ingot-height within the same ingots, and in comparison to the reference ingots. This is reflected in the solar cell efficiencies, which are reduced in the bottom and top, but are comparable to the reference at around 70% of the ingot-height.

The increasing defect concentration in the top of the Fe doped ingots may be related to the increasing iron concentration in the melt. In the bottom, the initial high concentration of Fe in the silicon melt may have induced a transient nucleation and growth disturbance during the early solidification phase.

Solar grade silicon feedstock specifications and conclusions (Chapter 5)

In the past several years discussion has taken place on the specifications for solar grade (SoG) silicon feedstock. The term SoG silicon feedstock dates back to the '70s at the beginning of the terrestrial use of photovoltaics during the oil crisis. It defines the particular type of feedstock suitable for the PV industry, as distinguished from electronic grade feedstock suitable for the microelectronic industry. Nowadays, 40 years later, there is still no final agreement on what this term should identify and even less agreement on the technical specifications.

In 2008 within the European Integrated Project *CrystalClear* a workshop entitled "Arriving to SoG silicon feedstock specification" was organized in Amsterdam on November the 13th and the 14th.

The most relevant aspect of a SoG feedstock, as concluded in the workshop, is related to the allowed levels of electrical dopants like B and P. Such dopants are essential to build a device, but they need to be controlled accurately. Hence, when present as unintentional impurities they may have major negative effects or even render materials unsuitable at completely. 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. UMG or direct route feedstock purification).

The next important aspect is the content of metal impurities in the feedstock. Many studies report that, despite of the higher level of metal concentrations, similar solar cell performance compared to electronic grade purity feedstock can be achieved. The 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 metal 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 the gettering processes.

A tentative and approximate standard set of specifications for solar grade silicon suitable for the fabrication of solar cells, resulted from the workshop discussion. Feedstock is divided into three SoG categories according to dopants (B and P) content. The general thought behind the categories proposed in Amsterdam is that they aim to identify the effect of the feedstock properties on the solar cell performance. It is therefore a differentiation relying on (assuming) suitable solar cell architectures and manufacturing processes. The advantage is that each item is specified in relation to its effect. Another approach to the specifications is 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 which do not fit exactly within predetermined categories. Also technology categories such as UMG, where feedstock characteristics may vary substantially from producer to producer, will be penalized. Many purification methods fall within this category, however, the content of dominant impurities and the overall feedstock purity differ considerably. The advantage of this approach is that it is relatively straightforward, but, on the

other hand, its usefulness for solar cell manufactures is limited, since the direct relation with cell performance is lost.

In both approaches, by downstream application and by purification technology, the specification for each impurity or class of impurities does 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 fact, in case slow diffusers are not present possibly higher level of faster diffusers are allowed and vice versa. In this respect the impurity class should be defined for those impurities having a similar effect on the solar cell performance. The studies reported in this thesis go in this direction, providing both the producers and consumers with information on the relative harmfulness of impurities and therefore allowing comparison of their quantities.

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

Samenvatting

Directe omzetting van zonne-energie in elektriciteit met zonnecellen is een snel groeiende technologie. Meer dan 80% van de wereldwijde zonnecelproductie is momenteel gebaseerd op silicium. In de afgelopen drie decennia hebben silicium fotovoltaïsche (PV) modules een prijsdaling van 20% voor elke verdubbeling van het cumulatief geproduceerde volume laten zien. De beschikbaarheid van silicium van (verondersteld) voldoende chemische zuiverheid ($>7\text{ N}$) is echter gedurende een deel van het afgelopen decennium een belangrijke beperkende factor geweest voor snelle groei en prijsdaling en zou dat in de toekomst weer kunnen worden. De zeer hoge investeringskosten die gemoeid zijn met conventionele siliciumproductie-eenheden vormt een barrière om dit probleem op te lossen en dit wordt nog hoger in tijden van financiële crisis. Alternatieve productieprocessen met een lager energiegebruik en daardoor een kortere energierugverdiensijd en kleinere koolstofvoetafdruk, gerekend naar het geproduceerde silicium, worden belangrijker als integrale duurzaamheid van energietechnologieën als ontwikkelingsdoelstelling wordt gekozen. Daarom bestaat er sterk behoefte aan technologieën met lage productie- en investeringskosten voor de fabricage van silicium voor PV-toepassingen. Zulke goedkope technologieën zullen echter waarschijnlijk een lagere zuiverheid silicium leveren. Het doel van de studies die in dit proefschrift worden gepresenteerd is om de complexe relatie te begrijpen tussen de zuiverheid van het silicium uitgangsmateriaal (de “feedstock”) en de prestaties van de zonnecellen die ervan worden gemaakt, rekening houdend met de invloed van de fabricageprocessen en het ontwerp van de cel.

Onzuiverheden in silicium: bronnen en vermindering van hun effect op zonnecelprestaties (Hoofdstuk 1)

Onzuiverheden worden geïntroduceerd en verwijderd tijdens de meeste stappen in de PV-moduleproductieketen. Het is belangrijk om op te merken dat kwarts, gebruikt als bron van silicium in feedstockproductie, niet de enige herkomst van onzuiverheden is. Belangrijke andere bronnen zijn de koolstofgebaseerde reductors die worden gebruikt voor de carbothermische productie van silicium (steenkool, cokes, houtskool of houtsnippers) en die calcium, fosfor, zwavel en metallische onzuiverheden in verschillende concentraties bevatten. De elektrodes en constructiematerialen van de ovens zelf brengen ijzer, chroom, nikkel en andere

metalen in het proces. Tot slot is het belangrijk om op te merken dat ook de vervolprocessen, kristallisatie en het zagen van plakken (wafers), onzuiverheden kunnen introduceren, bijvoorbeeld door de grafiet verhittelementen in Czochralski (Cz) en Directional Solidification (DS) ovens en door de materialen die in direct contact zijn met het silicium, zoals de kwarts containers en hun siliciumnitride coatings.

Segregatie gedurende de kristallisatie vermindert de concentratie van overgangsmetalen in het silicium aanzienlijk. Tijdens de diffusie van de emitter, het aanbrengen van de $\text{SiN}_x\text{:H}$ coating en de vorming van contacten vinden “gettering” (invangen) van onzuiverheden en passivering van (kristal)fouten plaats. Gettering van onzuiverheden is feitelijk een segregatieproces tussen twee vaste stoffen, in dit geval gedreven door de hogere oplosbaarheid van onzuiverheden in (bijvoorbeeld) de fosforrijke toplaag die fungeert als (zeer dunne) emitter in p-type siliciumplakken, die resulteert in het verwijderen van onzuiverheden uit het volume van de plak. Snel en relatief snel diffunderende onzuiverheden zoals ijzer, chroom, koper en nikkel kunnen op deze wijze worden verwijderd. Passivering van kristalfouten (puur kristallografisch of onzuiverheidgerelateerd) kan plaatsvinden tijdens het inbrengen van waterstof in het silicium gedurende specifieke processtappen, zoals tijdens de vorming van metaalcontacten, wanneer waterstof vanuit de waterstofrijke $\text{SiN}_x\text{:H}$ antireflectiecoating in het volume van de plak diffundeert.

Segregatie van onzuiverheden (Hoofdstuk 2)

Segregatiecoëfficiënten van onzuiverheden in silicium zijn over het algemeen kleiner dan één (dat wil zeggen dat onzuiverheden tijdens kristallisatie preferentieel in de smeltfase blijven) en nemen af met toenemende atoomafmetingen. Een uitzondering is zuurstof. Onder praktische kristalgroeicondities moeten normaliter *effectieve* segregatiecoëfficiënten worden gebruikt. De waarden daarvan worden beïnvloed door diffusie van onzuiverheden in de vloeistoffase, de dikte van de “grenslaag” en de kristalgroeisnelheid. Verder kan de verdeling van onzuiverheden in de siliciumkristallen worden beschreven door de normale stollingsvergelijkingen wanneer verdamping van onzuiverheden uit de vloeistof en vervuiling van de vloeistof of het kristal vanuit andere bronnen verwaarloosbaar is.

De rol van onzuiverheden in kristallijn silicium (Hoofdstuk 3)

Het zonnecel-energieconversierendement is direct gerelateerd aan het vermogen van de cel om elektron-gatparen die zijn gevormd door de absorptie van licht te collecteren (scheiden). Ladingsdragers die recombineren voordat ze geïncollecteerd

zijn dragen niet bij aan de stroomproductie van de cel. Recombinatie van ladingsdragers heeft ook invloed op de elektrische spanning die de cel kan opbouwen en bepaalt daarom in belangrijke mate het geproduceerde vermogen (het product van spanning en stroom) van de zonnecel. Diepe energieniveaus in de verboden band van silicium, veroorzaakt door kristalfouten en onzuiverheden, verhogen deze recombinitie en verminderen dus het geproduceerde vermogen en daarmee het rendement van de cel. Langzaam diffunderende onzuiverheden zoals titaan, molybdeen en vanadium moeten zoveel mogelijk uit het silicium worden gemeden omdat ze zeer moeilijk verwijderd kunnen worden met behulp van gettering. Snel of relatief snel diffunderende onzuiverheden zoals koper en ijzer zijn niet zo schadelijk, zelfs bij vrij hoge concentraties, omdat ze gegetterd kunnen worden, waardoor hun negatieve invloed op de zonnecelprestaties gedurende het fabricageproces aanzienlijk kan worden verminderd. Echter, door de aanwezigheid van kristalfouten (zoals dislocaties) kan het getteringeffect voor zulke onzuiverheden sterk worden verminderd omdat ze in het recombinitiegevoelige deel van de cel (het volume van de wafer) worden vastgehouden. Het Shockley-Read-Hall (SRH) model maakt het mogelijk om de invloed van onzuiverheden op de levensduur van ladingsdragers te voorspellen als de recombinitieparameters en foutenconcentraties bekend zijn. Om de invloed van onzuiverheden op het zonnecelgedrag te voorspellen moeten echter de concentraties van *elektrisch actieve* onzuiverheden bekend zijn, alsmede de afmetingen en verdeling van (eventuele) precipitaten (opeenhopingen) en de werkingscondities (injectieniveaus) van de zonnecel. Dit is een erg ambitieus doel en daarom zijn speciale studies naar de relatie tussen initiële onzuiverheidconcentraties in de feedstock en de uiteindelijke zonnecelprestaties nodig.

Invloed van metaalonzuiverheden op zonnecelprestaties (Hoofdstuk 4)

Het baanbrekende werk dat in de jaren '70 en '80 door het Westinghouse-team in de VS is uitgevoerd in het kader van het "Low cost solar array" (LCSA) project wordt nog steeds gebruikt als referentie voor de invloed van onzuiverheden op zonnecelprestaties. Dit onderzoek, vooral uitgevoerd op Cz monokristallijn silicium kristallen, had betrekking op een breed scala aan onzuiverheden. Het voornaamste resultaat van dit werk is een model dat de concentratie van onzuiverheden in silicium wafers, geschat uit hun effectieve segregatiecoëfficiënten, relateert aan (relatief) zonnecelrendement. Echter, door de enorme en vele verbeteringen in de zonnecelprocessen sinds die tijd, het toegenomen gebruik van DS multikristallijn silicium, het beschikbaar komen van krachtige rekenmiddelen en betere karakteriseringfaciliteiten bestond er behoefte aan geactualiseerde en meer gedetailleerde studies.

De auteur heeft in de afgelopen jaren het Westinghouse werk opnieuw gezien en een systematische studie uitgevoerd aan opzettelijk “vervuild” silicium en de effecten op zonnecelgedrag. Dit is gebeurd in het Europese Geïntegreerde Project *CrystalClear* en het Europese project *Foxy*. Belangrijke verschillen met het oudere werk zijn dat de nieuwe resultaten betrekking hebben op een modern, op zeefdruk gebaseerd industrieel zonnecelproces en op DS multikristallijn en FZ-materiaal in plaats van Cz-materiaal. In de nieuwe studies wordt een direct verband gelegd tussen, en een analyse gemaakt van, de onzuiverheidconcentraties in de feedstock en de uiteindelijke zonnecelprestaties. Dit geeft de meest directe en praktisch bruikbare interpretatie, in het bijzonder met het oog op het specificeren van toleranties ten aanzien van onzuiverheidconcentraties. De conclusies zijn daarmee ook niet afhankelijk van (aannames over) segregatiecoëfficiënten of detailanalyses van onzuiverheden.

Invloed van ijzer en molybdeen in zonnecellen van FZ-silicium (Hoofdstuk 4.1)

In dit werk wordt de rol bestudeerd van ijzer en molybdeen dat met opzet is toegevoegd aan de staven die worden gebruikt voor de fabricage van FZ-kristallen. FZ-kristallen kunnen worden gevormd uit mono- of multikristallijne zaadkristallen, met als resultaat mono- of multikristallijne staven. Dit maakt het mogelijk om de opname en invloed van onzuiverheden in de aanwezigheid van korrelgrenzen te bestuderen. “Landkaarten” van de levensduur van ladingsdragers in monokristallijn silicium wafers tonen een lateraal uniform beeld, waarbij de levensduur afneemt met toenemende concentraties van ijzer en molybdeen. Multikristallijne wafers laten gebieden met korte levensduren zien, overeenkomend met korrelgrenzen en dislocatierijke delen, die onafhankelijk zijn van de concentraties aan onzuiverheden. De levensduur *binnen* de korrels is hoger en varieert wel met die concentraties. Niet opzettelijk vervuild multikristallijn silicium kent kortere diffusielengtes van ladingdragers dan niet opzettelijk vervuild monokristallijn silicium, als gevolg van de recombinatie aan korrelgrenzen en dislocaties. In multikristallijn silicium heeft de laagst toegevoegde ijzerconcentratie (10^{12} at/cm³) nauwelijks invloed, terwijl de invloed van molybdeen al duidelijk zichtbaar is bij de laagste concentratie van 10^{11} at/cm³. In monokristallijn silicium wordt de diffusielengte van ladingsdragers al wel verkort door de laagste concentratie van ijzer. Dit heeft echter nog weinig gevolgen voor de zonnecelprestaties omdat de diffusielengte nog lang genoeg is om lichtgegenereerde ladingsdragers te collecteren.

Invloed van ijzer, chroom, nikkel, titaan en koper in multikristallijn-silicium zonnecellen (Hoofdstuk 4.2)

De invloed van de overgangsmetalen ijzer, chroom, nikkel, titaan en koper op zonnecelprestaties is onderzocht. Elke onzuiverheid is met opzet toegevoegd aan de feedstock die is gebruikt voor het maken van p-type DS multikristallijne siliciumblokken. De vervuilingniveaus zijn zo gekozen dat ze karakteristiek zijn voor de niveaus die mogen worden verwacht in (nieuwe) praktisch gebruikte materialen en om een duidelijk verschil te kunnen zien met onvervuild referentiemateriaal. Een modern zeefdrukgebaseerd proces is gebruikt om zonnecellen te maken van wafers uit alle delen (van onder tot boven) van de siliciumblokken. De aldus gemaakte zonnecellen zijn gekarakteriseerd en vergeleken met zonnecellen die van onvervuild referentiemateriaal zijn gemaakt, met het doel om zonnecelprestaties te correleren met onzuiverheidsniveaus. Toevoeging aan de feedstock van 50 ppm (op gewichtsbasis; ppm wt) ijzer of 40 ppm wt nikkel of chroom leidt tot zonnecelprestaties die vergelijkbaar zijn met de referentie voor wafers die uit het deel tussen 40% en 70% van de hoogte van het blok afkomstig zijn. Toevoeging van 10 ppm wt titaan verlaagt de zonnecelprestaties drastisch voor wafers uit alle delen van het blok. Onzuiverheden zoals ijzer, chroom en titaan veroorzaken een verkorting van de diffusielengte van ladingsdragers in het *volume* van de wafers. Nikkel heeft daarop geen invloed, zelfs niet bij de hoogste concentratie van 200 ppm wt. Daarentegen heeft nikkel wel grote negatieve invloed op de recombinatie in de emitter en daarmee ook op de zonnecelprestaties. Koper heeft de bijzondere eigenschap om recombinatie in zowel in het volume van de wafers als in de emitter te beïnvloeden.

Er zijn twee modellen ontwikkeld om de gemeten (degradatie van) zonnecelprestaties over de lengte van het siliciumblok te beschrijven, gebruikmakend van de verdeling van onzuiverheden volgens de Scheil-functie. Het zonnecelgedrag is gemodelleerd als functie van volume- en emitterrecombinatie. De modellen beschrijven de experimenteel verkregen gegevens goed en zijn met succes toegepast op siliciumblokken met verschillende onzuiverheidsconcentraties. In tegenstelling tot de verwachting laat de Scheil-verdeling van onzuiverheden over het siliciumblok zelfs zijn vingerafdruk na aan het einde van het zonnecelproces.

Het model is gebruikt om de schadelijkheid van onzuiverheden te classificeren en om de invloed van zekere hoeveelheden aan onzuiverheden in de feedstock op zonnecelprestaties te schatten. Als een maat voor (nog acceptabele) concentraties is gekozen voor de waarde waarbij de relatieve afname van de prestaties minder dan 2% is over minimaal 90% van de blokhoogte. Dit relateert de concentratie van onzuiverheden direct aan zonnecelgedrag en is niet afhankelijk van kennis over effectieve segregatiecoëfficiënten, invangstdoorsneden voor recombinatie en

specifieke elektrische activiteiten van onzuiverheden, omdat alleen het totaaleffect de parameter in het model is. Het gevonden resultaat is dat 8 ppm wt chroom, 11 ppm wt ijzer, 0,1 ppm wt titaan, 4 ppm wt nikkel en 8 ppm wt koper een gelijk(waardig) negatief effect op de zonnecelprestaties hebben. Het voordeel van deze aanpak is dat alle fysisch/chemische eigenschappen van een onzuiverheid worden gevat in een enkele parameter die eenvoudig kan worden vergeleken.

Invloed van ijzer in p-type en n-type multikristallijn-silicium zonnecellen (Hoofdstuk 4.3)

Ongeveer 50 ppm wt ijzer is toegevoegd aan silicium feedstock vóór het smelten en vervolgens kristalliseren van p-type en n-type gedoteerde blokken. De verschillen in de levensduur van ladingsdragers direct na kristallisatie tussen p-type (1-2 μ s) en n-type (6-20 μ s), met ijzer vervuilde siliciumblokken kunnen worden verklaard met de SRH-theorie voor fouten ten gevolge van interstitieel ijzer. Sommige korrelgrenzen blijken te fungeren als “put” voor onzuiverheden, resulterend in een schoner gebied rondom die grenzen, met langere levensduren van ladingsdragers. De concentratie aan interstitieel-ijzergelateerde fouten $[Fe_i]$ in nieuw gevormd p-type materiaal is in de orde van grootte van 10^{13} at/cm³, wat overeenkomt met ongeveer 10% van de totale ijzerconcentratie. Fabricageprocessen voor p-type en n-type silicium wafers zijn gebruikt om zonnecellen te maken van ijzervervuild materiaal en schoon referentiemateriaal. Fosfordiffusie en waterstofpassivering verlengen de levensduur van ladingsdragers met een factor 50 voor p-type ijzervervuild materiaal en een factor 5 voor n-type materiaal. Door codiffusie van fosfor en borium neemt de levensduur toe met een factor 10 voor p-type materiaal en een factor 4 voor n-type materiaal. De $[Fe_i]$ neemt af van 10^{13} at/cm³ tot 10^{11} at/cm³ in p-type materiaal door fosfordiffusie. Na fosfor/borium codiffusie en waterstofpassivering is $[Fe_i]$ ongeveer 10^{12} at/cm³, wat het ijzergetteringeffect van het diffusieproces bevestigt.

De concentratie van interstitieel ijzer na uitvoering van het zonnecelproces (fosfordiffusie en waterstofpassivering) volgt een concentratietrend langs de hoogterichting van het siliciumblok die ongeveer in overeenstemming is met de Scheil-functie. De afname van de diffusielengte is eveneens consistent met de Scheil-verdeling van actief ijzer. De metingen laten verder waterstofpassivering van korrelgrenzen en gebieden met hoge concentraties aan dislocaties zien.

Er is een verschil in de ontwikkeling van de kristalstructuur gedurende kristallisatie voor beide ijzervervuilde blokken in vergelijking met het referentieblok. De concentratie kristalfouten in de onderste en bovenste delen is in de ijzervervuilde blokken verhoogd, zowel ten opzichte van de concentratie op ongeveer 70% van de hoogte van dezelfde blokken als in vergelijking met de referentieblokken. Dit is ook

zichtbaar in de zonnecelprestaties, die lager zijn voor materiaal uit de onderste en bovenste delen, maar vergelijkbaar zijn met de referentie op ongeveer 70% van de hoogte. De hogere foutenconcentratie in het bovenste deel van het blok kan het gevolg zijn van de toenemende ijzerconcentratie in de vloeistoffase tijdens de kristallisatie. In het onderste deel kan de hoge ijzerconcentratie invloed hebben gehad op nucleatie en groei in het eerste fasen van het kristallisatieproces.

Specificaties van “zonnekwaliteit” silicium en conclusies (Hoofdstuk 5)

In de afgelopen jaren is er discussie geweest over de specificaties van “zonnekwaliteit” (solar grade) silicium feedstock. De term “zonnekwaliteit” heeft zijn oorsprong in de jaren '70; de beginperiode van aardse toepassingen van zonnecellen tijdens de oliecrises. De term definieert de specifieke kwaliteit silicium die geschikt (geoptimaliseerd) is voor de PV-industrie, in tegenstelling tot halfgeleiderkwaliteit-silicium voor de micro-elektronica-industrie. Vandaag, 40 jaar later, is er nog steeds geen overeenstemming over wat de term “zonnekwaliteit” precies zou moeten inhouden en nog minder over de kwantitatieve specificaties.

In 2008 (13-14 november) is in het kader van het Europese Geïntegreerde Project *CrystalClear* in Amsterdam een workshop georganiseerd onder de titel “Arriving to solar grade silicon feedstock specification”. Het meest relevante aspect van een “zonnekwaliteit” feedstock, zo werd geconcludeerd tijdens de workshop, is gerelateerd aan toelaatbare concentraties van elektrisch actieve onzuiverheden (doteringen) zoals borium en fosfor. Zulke onzuiverheden zijn essentieel om een zonnecel te maken, maar hun concentratie moet nauwkeurig kunnen worden gecontroleerd. Als deze elementen aanwezig zijn als onbedoelde onzuiverheden kunnen ze sterk negatieve invloed hebben of materiaal zelfs volledig onbruikbaar maken. Vanwege hun segregatie-eigenschappen kan hun concentratie niet of moeilijk worden verlaagd tijdens het kristallisatieproces. Verder is het erg moeilijk om ze te verwijderen tijdens de feedstockproductie voor technologieën die niet zijn gebaseerd op gasfasezuivering, zoals Upgraded Metallurgical Grade (UMG) silicium.

Het volgende belangrijke aspect is de concentratie van metaalozuiverheden in de feedstock. Veel studies laten zien dat zelfs uit materiaal met hogere concentraties van zulke onzuiverheden zonnecellen kunnen worden gemaakt met prestaties die vergelijkbaar zijn met referentiecellen. De fysische eigenschappen van zulke onzuiverheden zijn daarbij bepalend. Parameters die met name het verschil maken zijn de diffusie- en segregatiecoëfficiënten. Dit geeft aanleiding tot de definitie van klassen (categorieën) van metaalozuiverheden: snel diffunderende onzuiverheden zijn minder schadelijk dan langzaam diffunderende omdat ze makkelijker kunnen worden gemanipuleerd door gettering tijdens celfabricage.

De workshop heeft een voorlopige en enigszins grove standaard set van specificaties voor “zonnekwaliteit” silicium opgeleverd die bruikbaar is voor de fabricage van zonnecellen. Zonnekwaliteit silicium feedstock kan worden onderverdeeld in drie categorieën gerelateerd aan de concentraties dotingen (borium en fosfor). De algemene gedachte hierachter is dat de categorieën directe relevantie moeten hebben voor zonnecelfabricage, aannemende dat er geschikte celprocessen en –ontwerpen worden toegepast. Het voordeel is dat elk onderdeel wordt gespecificeerd in relatie tot zijn effect. Een andere aanpak is om de verschillende feedstocks te classificeren naar de zuiveringsmethode die gebruikt is voor fabricage. Dit heeft duidelijke voordelen voor de gevestigde technologieën (zoals het Siemensproces), maar heeft nadelen voor nieuwe technologieën die nog niet in een bepaalde categorie vallen. Ook technologieën zoals UMG, waarvoor feedstock-eigenschappen aanzienlijk kunnen variëren van producent tot producent zouden kunnen lijden onder zo’n classificatie. Veel zuiveringsroutes vallen binnen deze categorie, maar de concentraties aan belangrijke onzuiverheden en de totale zuiverheid van het materiaal verschillen sterk. Het voordeel van deze aanpak is dat hij relatief recht-toe-recht-aan is, maar de bruikbaarheid voor zonnecellenfabrikanten is beperkt omdat er geen directe relatie met celprestaties bestaat.

In geen van beide benaderingen, naar toepassing of naar zuiveringstechnologie, dekken de specificaties per onzuiverheid of klasse de volledige ruimte van mogelijke invloeden. Bijvoorbeeld, de definitie van een maximum concentratie aan langzaam diffunderende onzuiverheden *tezamen* met snel diffunderende onzuiverheden is een veilige specificatie. Echter, wanneer de eerste niet aanwezig zijn zou een hogere concentratie van de tweede toelaatbaar zijn, en omgekeerd. Daarom zouden de concentraties bij voorkeur per type onzuiverheid met vergelijkbare effecten op zonnecelprestaties moeten worden gespecificeerd. De studies beschreven in dit proefschrift gaan in die richting en geven zowel producenten van feedstock als gebruikers ervan informatie over de relatieve schadelijkheid van onzuiverheden, waarmee een zinvolle vergelijking van concentraties mogelijk wordt.

Om te komen tot volledige en volledig bruikbare specificaties is het nodig om ook de invloed van andere onzuiverheden te onderzoeken, alsmede de interacties tussen onzuiverheden onderling en (in meer detail) tussen onzuiverheden en kristalfouten.

About the author



Gianluca Coletti (1975) is currently senior scientist at the Energy research Centre of the Netherlands (ECN). He studied physics at the university of Rome "La Sapienza", Italy, where he graduated in 2001 with a thesis on the "Characterisation of Crystalline Silicon Solar Cells in the Production Process". From 2000 to 2001 he carried out his thesis research work at Eurosolare S.p.A., (Eni Group) in Rome, Italy. In 2001, he received a research grant from Eurosolare S.p.A. on the "development of innovative technologies for silicon solar cells". In 2004 he received another research grant from ENEA (Italian national agency for new technologies, energy and sustainable economic development) but shortly after accepted a position as project leader at ECN and moved to The Netherlands.

Since 2004 he works at ECN, leading research projects in the area of solar cell technology, Si material and industry technology transfer. From 2005 to 2009, he coordinated the feedstock-related program of CrystalClear (a large European project) on the impact of feedstock, ingot and wafer quality on solar cell performance. Very important results, invited talks at international conferences and publications in several peer reviewed journal papers have been obtained under his coordination. He has more than 10 year experience in PV with more than 40 publications in various international level journals and conference proceedings. He organized a well received and frequently cited 2 days workshop on "Arriving to solar grade silicon feedstock specifications" held in Amsterdam on 13-14 November 2008. Gianluca Coletti is considered a leading expert in the area of silicon material for PV. In 2009 and 2010 he was visiting scientist at the Australian National University (ANU) in Canberra, Australia and at the National Renewable Energy Laboratory (NREL) in Golden, Colorado, USA, where he worked on silicon material related topics. Gianluca Coletti is member of the SEMI PV Silicon Material Task Force. Currently he is coordinating the PV silicon material research program at ECN Solar Energy and he is project manager of large research projects (>2 MEuro) among which a project aiming to develop new technology for high efficiency silicon solar cells.

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