Date: November, 2009
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Doc Ref No: R0110

Impurities in silicon photovoltaic cells

Context

Solar cell market is showing a remarkable growth, at + 40%/year average. Silicon-based technologies are about 85% of the market, and are helped by the 2009 dropping prices for high grade silicon. It is essential for AL to position itself in the various phases of the cell manufacturing process. Impurity-related constraints are critical, considering the high grade and the amount of gas to be supplied.

Objectives

The goal of this study is first to give an overview of the impurity-induced degradations in silicon solar cells, and when possible, to link them with the purity requirements of PV gas precursors. The background goal is also to identify new gas treatment technologies in solar-cell manufacturing, such as passivation-treatments, gas deposition, or gas cleaning treatments.

Results and conclusions

The tolerance to impurities in a PV cell is mostly linked to the amount of electron-hole recombinations induced by the impurities, and hence to the minority-carrier (MC) lifetime. For both crystalline and amorphous cells, the minimum lifetime is around 10 µs. Most detrimental impurities (typically 3d transition metals) have tolerance levels as low as 10 ppt (concentration of active impurities within the cell). Substitutional impurities in Si, among which many acceptors and donors, are also critical because of the difficulty to segregate them from silicon.

Inside the PV-active silicon, MC lifetime is in fact improved by chemical passivations (in particular by hydrogen, oxygen, or carbon), or by dangling-bound passivation (in amorphous Si). During processing, impurities can also be removed or de-activated by thermal diffusion and precipitation, or by more complex gettering techniques. In addition, there occurs contaminations and segregations during the making process (diffusion, evaporation, liquid treatments, atmospheric pollution,…). All these effects must be considered to determine the actual gas feed requirements.

In Si wafer manufacture, the natural segregation induced by crystallization is efficient against most transition metals, but not against substitutional elements. Silicon purity requirement at pre-wafer step (silicon precursor purity) is estimated around 10 ppb and is mostly limited by substitutional impurities.

For thin film manufacturing, experimental data is scarce. Common gas impurities have mild specification requirements (tens of ppm and above). In CVD, oxygen and nitrogen tolerance levels may be reached due to low base-pressure requirements (air contamination). In contrast to wafer cells, there is no crystallization-induced segregation, but there is gas-phase segregation and more passivation effects (from hydrogen and dangling bonds) within the cell.

Key words

Impurity, photovoltaics, solar cell, silicon

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1. Introduction

The tolerance to an impurity within a photovoltaic (PV) cell first depends on the degree of the electronic perturbation induced by the impurity. This is determined by the affinity of the impurity for the charge carriers, and hence varies with each element. We will show that the tolerable-amount of impurities is different by several orders of magnitude along the table of elements, with some element (transition metal in particular) being detrimental at very low concentration level (ppt).

To quantify the requirements on the gas feed, it is also necessary to relate the gas feed purity to the concentration of impurities which are finally active within the cell. There are segregation phenomena, purifying or polluting the cell, during manufacture. There are also several passivation-effects that de-activate the impurities. For this reason, the purity requirements of the gas feed strongly depend on the cell fabrication process.

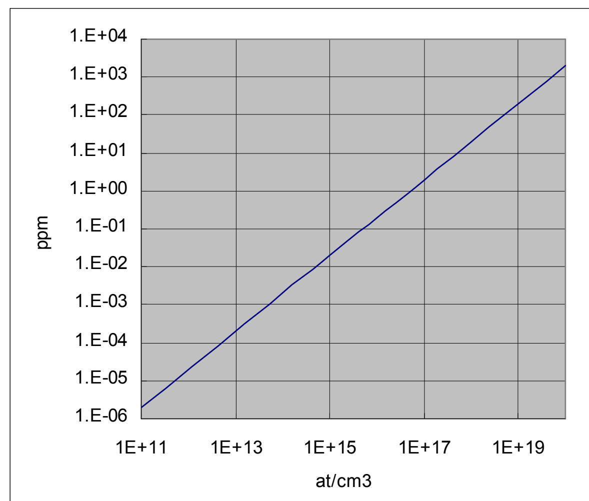

Fig. 1: Unit conversion between ppm and at/cm3

2. Electronic perturbation by an impurity

2.1. Minority-carrier (MC) diffusion length and lifetime

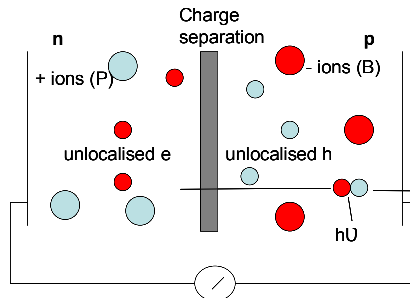

Fig. 2: Principle of a mono-junction PV cell. Blue: positive charge, Red: negative charge, Large circle: static ions, Small circle: charge carriers

The principle of a semi-conductor PV cell is to photo-induce electron-hole pairs, and separate these charges at the two sides of a junction. To carry this separation efficiently, it is essential that the minority carrier (MC) has a sufficient diffusion length (δ) before an electron-hole recombination occurs. Practically, diffusion length must be comparable to cell thickness.

Diffusion length is determined by MC lifetime, and governed by the basic diffusion law:

$\delta = (D.\tau)^{1/2}$, with D the diffusivity of electrons between recombination centers (this is an indicator of charge mobility).

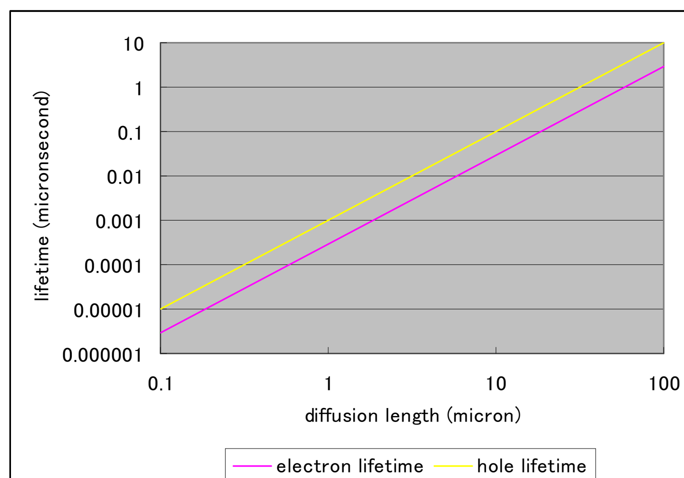

Fig. 3: Conversion between lifetime and diffusion length in a lightly doped wafer at room temperature (D = 35 cm^2/s for electrons, D = 10 cm^2/s for holes).

2.2. Electronic perturbation by the elements

Neutrals
Donors
Acceptors
Lifetime killers

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Period 1	H																
Period 2	Li	Be											B	C	N	O	F
Period 3	Na	Mg											Al	Si	P	S	Cl
Period 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Period 5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Period 6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At

Table 1: The influence of elemental impurities in silicon. red: detrimental, yellow: rather detrimental, green: neutral or favorable

The main effect of impurities is to create local bounding states which may be temporary traps which reduce D, or efficient electron-hole recombination-centers which reduce τ.

2.2.1. Neutral impurities

Goup IV (C, Ge, Sn) impurities are electrically neutral and tend to be substitutional in the Si lattice. They do not affect PV properties at "impurity" levels. Only at alloying level (% levels), can IV elements distort the Si lattice, and consequently distort the reciprocal space and band gap.

For instance, we have already seen in a previous report [T. Laude, Tin precursors for PV, AL R0409 (2009)] that the degradation of photovoltaic properties with Sn inclusion occurs at % levels. Lighter elements such as Ge have higher solubility than Sn in Si, and hence can be better tolerated. In fact, SiGe alloy is widely studied as an infrared direct band gap material.

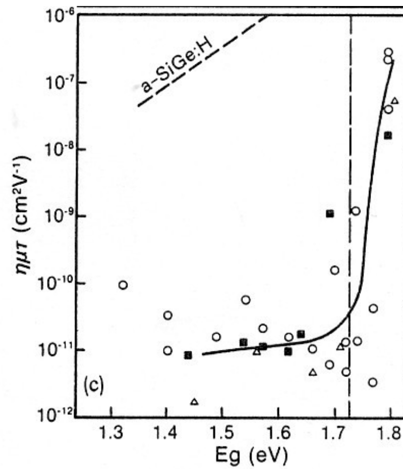

Fig. 4: Degradation of the photoresponse in a-Si:H with 0 to 10 % Sn content (on horizontal axis, Sn content decrease linearly with Eg). [Mahan]

Similarly, any impurity that causes no local state with energy within the band gap, can be considered as electrically neutral. This is the case of hydrogen for instance.

2.2.2. Donor and acceptor (dopants) impurities

Donors and acceptors (dopants) impurities induce a shallow state in the band gap, within 0.05 eV of the conductive or valence band. Such impurities are mostly ionized by thermal excitation at room temperature, and are therefore ionic impurities. They are often substitutional in the Si lattice. These include group III (B, Al, Ga, in) and group V (N, P, As, Sb), but also other elements such as O and N (mild donors).

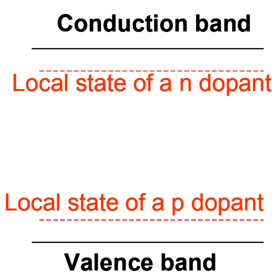

Fig. 5: Energy levels of donor and acceptor states within the Si band gap

The electronic perturbation to the MC induced by those impurities is typically modest below the ppm level. This is because they only act as temporary traps, not as recombination centers. Even ions with charge opposing the main doping (“compensating doping impurities”), which have a specific affinity for the MCs, cause no severe degradation to photovoltaic properties [D. Macdonald et al.].

On the other hand, over a certain level, typically the ppm level, these impurities induce a severe MC lifetime drop (see figure), and hence impede any photovoltaic effect. This is due to an indirect

recombination process (Auger-recombination process), that is triggered by interactions between majority carriers.

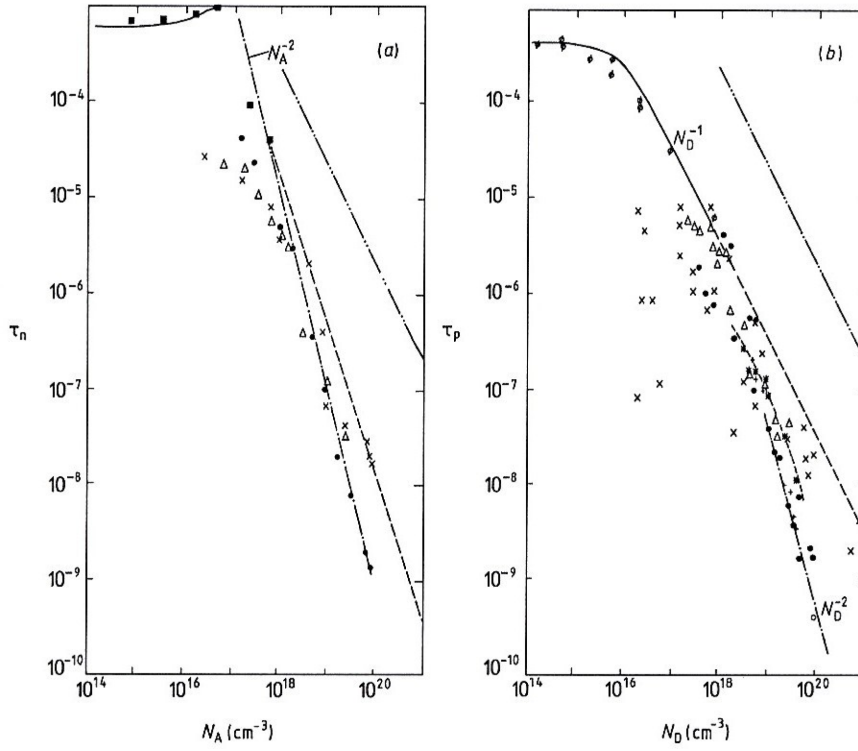

Fig. 6: Lifetime as a function of doping density in p type (left panel) and n type (right panel) silicon. At high doping densities the lifetime varies like the inverse square of the doping density, indicating that Auger processes are dominant. Lifetime for other recombination processes are expected to vary like the simple inverse of the doping. [Physics of solar cell p. 184, quoted from Van Overstraeten 1986]

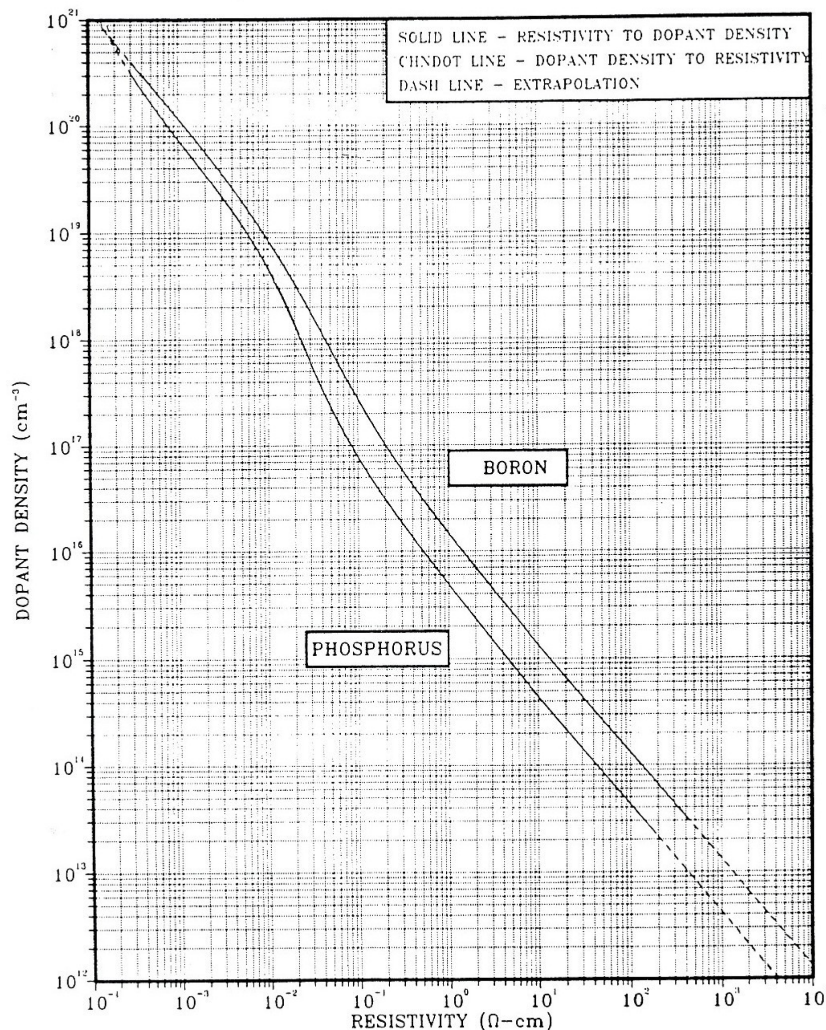

Fig. 7: Preferred conversion between resistivity and total dopant density values for boron and phosphorus-doped silicon

2.2.3. Lifetime killers

Lifetime-killers are impurities inducing a direct recombination of electrons and holes ("Shockey Read Hall" recombination). This occurs only if the impurity has affinity for both carriers. This is typically linked to the presence of a deep state near the middle of the band gap [Physics of solar cells].

A group of lifetime killers is well identified at the left part of the transition metal, Ta, Mo, Nb, Zr, W, Ti, V (3d, 4d, and 5d orbital groups). PV tolerance levels (concentration of active impurities within the cell) as low as 10 ppt are reported (see figure). Transition metals have unfilled d orbital which enables various bonding with the silicon lattice.

Lifetime-killers impurities being active recombination centers, the MC lifetime is inverse-linear with impurity concentration: $\tau = 1 / (v.\sigma.N)$, where N is the impurity concentration, σ is the MC-defect effective collision surface, and v is the MC velocity (2×10^5 m/s for electrons at room temperature).

Note: This expression is not obvious. It suppose that the recombination rate is limited by the ballistic capture of carriers from the region surrounding the impurity (at a distance equal to the mean free path of electron-lattice collision), and not by the drift velocity of the carrier between impurities.

As shown on the figures below, the reduction of cell efficiency in a mono-crystalline cell is extremely severe for transition metals of period 4, 5 and 6 (Ta, Mo, Nb, Zr, W, Ti, V). The tolerance is as low as 10^{11} at/cm^3 (1 ppt). On the other hand, transition metals from period 10 or 11 such as Cu (<0.1 ppm) and Ni (<0.01 ppm), are relatively well tolerated in the PV material. This difference is first attributed to a different diffusivity in c-Si (Cu and Ni have high diffusivity and migrates out of the PV active zone, or precipitate on cooling). It is thought that the measured perturbation for Cu or Ni is due to the fraction of Cu atoms that are substitutional and not interstitial in Si, and thus do not diffuse well.

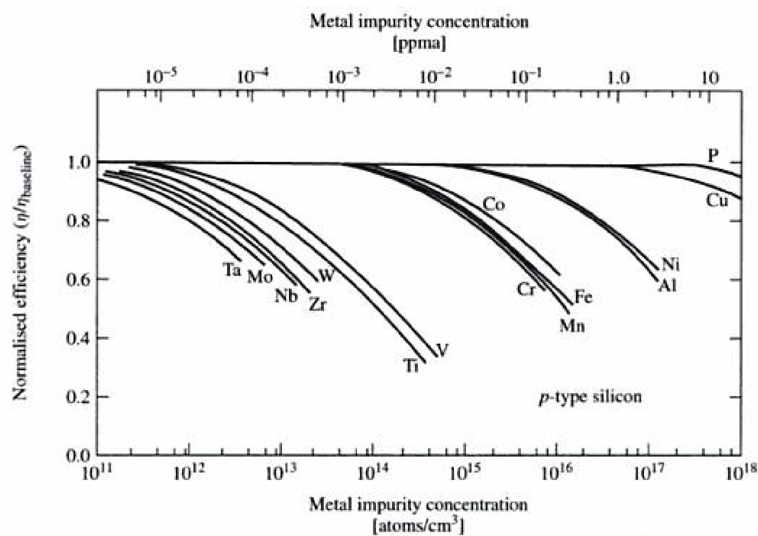

Fig. 8 Solar cell efficiency versus impurity concentration for 4 ohm cm p-base Cz Si devices. [Davis Jr. J et al., IEEE trans Electron Devices (1980)]

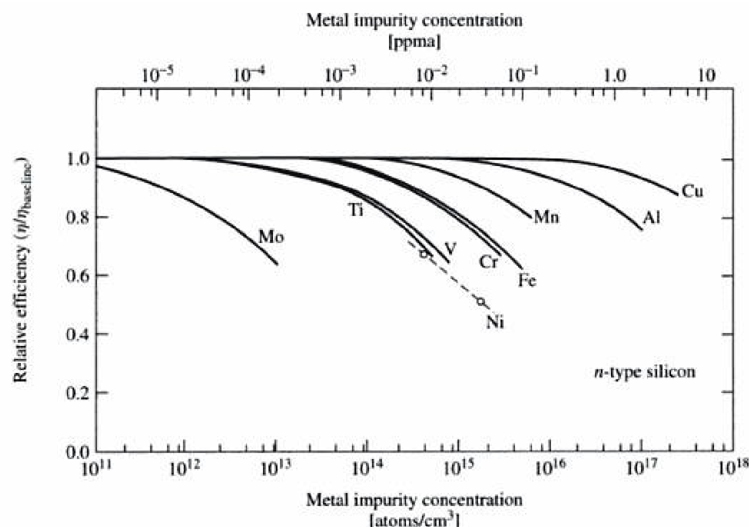

Fig. 9 : Solar cell efficiency versus impurity concentration for 1.5 ohm cm n-base Cz Si devices. [Davis Jr. J et al., IEEE trans Electron Devices (1980)]

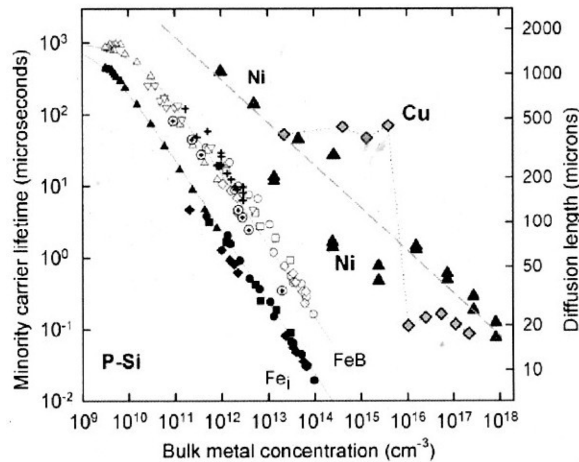

Fig. 10: Impact of iron, copper, and nickel on minority carrier diffusion length in single-crystalline silicon. The shaded area represents a typical range of minority carrier diffusion lengths in multi-crystalline silicon solar cells. [Istratov]

2.3. Common impurities

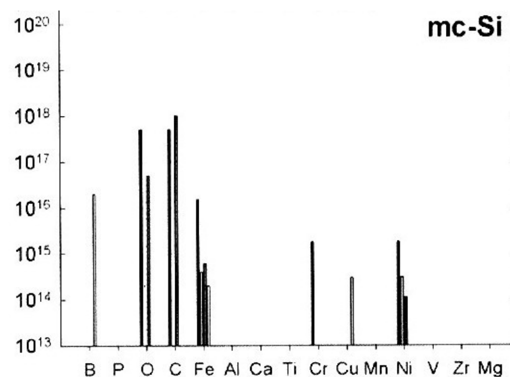

Fig. 11: Impurity amount measured in several multi-crystalline Si wafer [Istratov]

2.3.1. Oxygen and nitrogen (mild donor, interstitial)

Oxygen is a common impurity in wafer-based cells which arises mostly from the wafer crucible. Oxygen and nitrogen are common impurities in thin film cells which arise from air contamination in large-scale deposition systems. Fortunately, the PV tolerance to O and N in the cell is relatively high. For instance, tolerance was estimated O: 2.10^{19} atom/cm^3 (400 ppm) ; N: 4.10^{18} atom/cm^3 (80 ppm) in a-Si:H cells [J. Woerdenweber et al, J. of Appl Phys 104 094507, 2008]. See also paragraph 3.3.2.

In wafer-based c-Si cell, oxygen is found below 10^{18} atom/cm^3 (20 ppm), which is also the oxygen solubility in Si at Si-melting temperature. Oxygen is known to precipitate as SiO2 on silicon cooling

(oxygen has a high diffusivity in c-Si). Therefore, oxygen content in c-Si cell is not a problem in itself. Oxygen and nitrogen are more troublesome in thin films, as O and N from air leaks are quenched in the depositing Si (see gas purity levels in part 3.3.2).

The indirect effect of oxygen by complexation with other elements is debated. It is thought that oxygen has a favorable passivation effect on metallic impurities (internal oxygen gettering), but on the other hand, the boron-oxide complex in boron-doped wafer is suspected to be detrimental.

2.3.2. Carbon (neutral, substitutional)

A high level of carbon is also common due to several contaminations during cell manufacturing, namely from steel equipment and from organic chemicals. As already discussed, carbon has no direct influence on PV properties at ppm levels. On the other hand, carbon has a strong affinity for Fe, and therefore helps to passivate its negative effects.

Similarly to oxygen, for wafer based c-Si cells, carbon solubility in Si at Si-melting temperature is limiting at 3.5 10^{17} at/cm^3 (7 ppm), and carbon readily form SiC precipitates on Si cooling.

2.3.3. Hydrogen (neutral, interstitial)

Hydrogen being an excellent passivator, it is usually introduced intentionally in the cell. Hydrogen is well tolerated in the cell, up to %at levels. It can passivate either positively or negatively charged impurities/defects, in particular dangling bounds in a-Si:H, or metal impurities [Lauwaert] [Stavola].

Hydrogen is first used in a-Si cells, although hydrogen is partly out-gazed from a-Si:H cell on usage, due to high diffusivity and weak bounding. Light exposure typically causes a 30% efficiency-loss during the first month of usage (Staebler Wronski effect). Hydrogen is also used in multi-crystalline wafer cell manufacture.

3. Purity requirements

3.1. Different types of silicon cells

3.1.1 The wafer c-Si cells and the monojunction amorphous cell

The two historical silicon cells (which are still dominant in the market today) are the mono-junction wafer-based c-Si cells (including mono-crystalline, multi-crystalline and ribbon types) which is

crystallized near Si-melting temperature (1414 C), and the mono-junction a-Si:H cell, usually grown by silane PECVD at low temperatures.

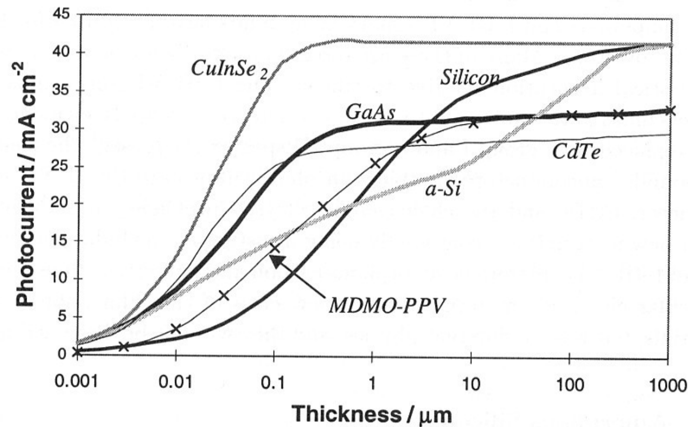

Fig. 12: Maximum photon current available from each material under AM1.5 illumination, as a function of film thickness, assuming perfect collection of all photogenerated charges. The saturation photocurrent is a function of band gap. The maximum photocurrent supplied by the AM1.5 spectrum is around 49 $mAcm^{-2}$. [The physics of solar cells, p. 214]

One essential difference between crystalline and amorphous silicon, is that c-Si is a relatively poor absorbing material (due to its indirect band-gap), when a-Si has reasonably good absorption properties (see figure). As a result, for c-Si, the PV active layer must be thicker than 100 μm to absorb most incident energy. A typical wafer based c-Si cell is 100-300 μm thick. Fortunately, thanks to high crystallinity, c-Si allows long MC diffusion length (mono-crystalline cells are better than multi-crystalline cells in this respect), exceeding this absorption distance, and c-Si cell efficiency can be high (typically close to 20% for commercial wafer-based Si cells).

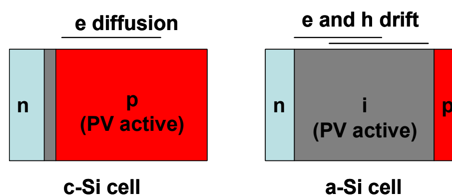

Fig. 13: Typical designs for wafer-based mono-junction c-Si cell, and mono-function a-Si:H cell designs

Typical wafer c-Si cell design:

- p-n junction

- Boron (p) doping is set around 10^{16} at/cm^3 (0.5 ppm). This allows a MC lifetime over 10 microseconds, and maximizes electrical conductivity.
- Phosphorus (n) doping (from POCl3), is set around 10^{19} at/cm^3 (300 ppm), which effectively kills the lifetime (n doped Si is PV inactive). However, this is favorable because the n-doped layer is also thin (transparent). Optical absorption is confined in the p layer near the junction, and the n layer enables good electrical conduction.
- Other doping impurities are typically maintained below the 10 ppb level in the PV active zone, to avoid a perturbation to the main doping.

For a-Si, the defective nature of amorphous Si causes a short MC diffusion length (typically 0.1 µm). As a result, layer thickness must be limited to around 0.3 µm (carrier diffusion is enhanced by charge drift in the junction). Hence, only part of the spectrum is absorbed, and cell efficiency is roughly half that of c-Si.

A typical a-Si cell uses a n-i-p junction, the light being absorbed in the central intrinsic (non-doped) region. This design enables the electrical drift of carriers in the junction field, and solves the problem of doping a-Si (a-Si doping is not efficient, and hence must be dense, at the cost of a short MC diffusion length). Note that in a-Si cell, light must be incident on the p-doped side, due to different mobility of electron and holes.

3.1.2 HIT cell

The HIT cell (heterojunction with intrinsic with layer) produced by Sanyo is somehow a a-Si/c-Si hybrid. A thick n-doped c-Si layer is sandwitched between ultra-thin (10-20 nm) a-Si layers (see figure). Owning to their thinness, the amorphous layers are almost transparent, and hence, only the c-Si is PV active. Therefore, from a purity perspective (MC perspective), the purity requirement of the HIT cell are the same as other wafer based c-Si cells. The purity requirement for the amorphous Si region (deposited from silane) is not critical as long as impurities do not migrate to the PV active zone.

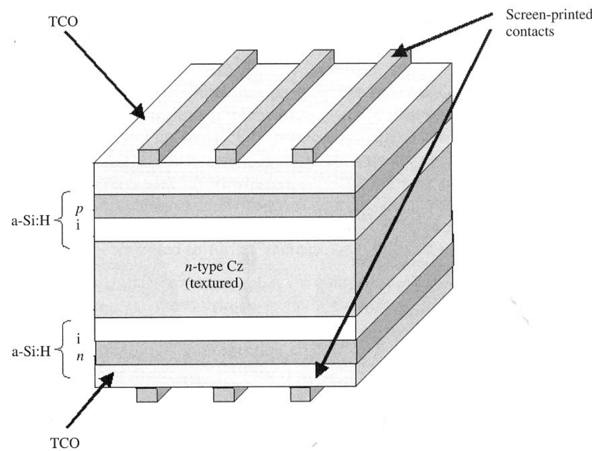

Fig. 14: The Sanyo HIT cell [Handbook of photovoltaic science and engineering, p.289]

3.1.3 micro-crystalline Si cell

As a recent evolution to the traditional mono-junction a-Si cell, a new material, micro-crystalline Si (μc-Si, also called nano-crystalline Si), has been developed. μc-Si is a semi-crystalline material, best described as an amorphous Si matrix containing Si nanocrystals, hence with optical properties in between amorphous and crystalline Si (see figure). μc-Si enables a better trade off between light absorption and MC diffusion length, in the low energy part of the spectrum.

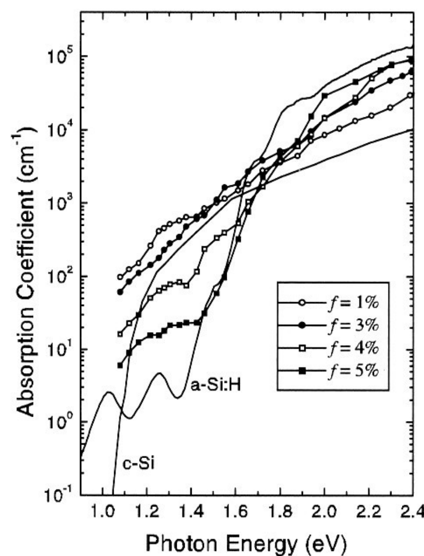

Fig. 15: Absorption spectra for thin films deposited at different silane concentration (hence different levels of crystallinity) in comparison with the spectra of standard c-Si and a-Si:H. [Ambrosone]

μc-Si is been developed in particular as the bottom cell in a-Si:H/μc-Si:H multi-junction cell design (see figure). Typical layer thickness is 1-2μm, which corresponds to the typical MC diffusion length obtained in μc-Si (one order of magnitude better than a-Si thanks to crystallinity). This is typically

grown by PECVD at low temperature (100-300C) by adding a large hydrogen dilution to silane (hence slower growth than a-Si).

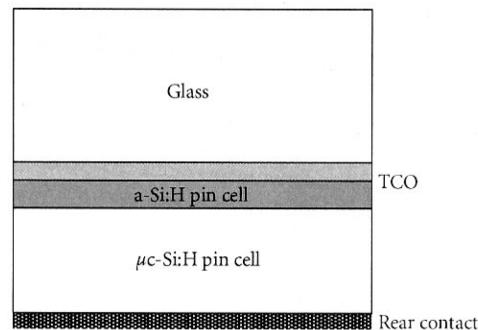

Fig. 16: Schematic drawing of a a-Si:H/μc-Si:H multi-junction cell [Beaucarne]

3.1.4 Low T polycrystalline Si cell

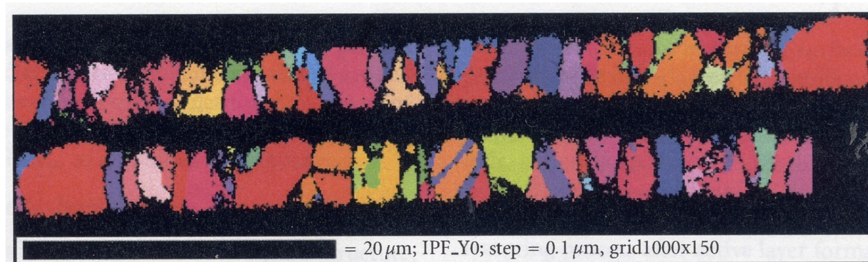

Fig. 17: Electron microscope image of polycrystalline Si layer (upper image is continued on lower image) [Beaucarne]

A third example of the evolution of PV cell manufacturing is the development of low temperature grown "polycrystalline" cells. These cells are fully crystalline, but grown at low temperature. Usually the crystal is grown by crystallization of a CVD-deposited a-Si layer. Typical temperature is 600C, and results of a trade off between the need for larger grains (lower temperature is better) and the need for a faster process (higher temperature is better).

To avoid grain boundaries losses, a polycrystalline silicon film is grown with only one grain through layer depth. This depth is limited to the best MC diffusion length obtained, a few microns at present. Owning to the mediocre absorption of c-Si (see figure), a few micron thickness implies that only half of the light is absorbed. Cell efficiency around 10% has been reported. Obviously, an increase of the MC diffusion length of polycrystalline Si would enable a breakthrough in this field.

3.2. Purity requirements for wafer based c-Si cell

3.2.1. Effect of Si crystallization on Si purity

For crystalline silicon cells, crystallization is a natural purification mechanism, the incorporation of impurities from the liquid phase being limited by incorporation energy barriers. The segregation coefficient (equilibrium ratio of impurity concentrations between liquid and crystal phases in slow growth condition) being very low for most impurities, it is a very efficient way to purify silicon. This natural purification is more efficient for mono-crystalline Si cells than for multi-crystalline Si cells, due to a slower crystallization and better control of the liquid Si phase.

Note: During crystallization, the segregated-impurities accumulate in molten Si. They eventually deposit on the growing wafer at a saturation concentration. In multi-crystalline wafering, impurities accumulate at grain boundaries, where they should be etched or passivated. In mono-crystalline wafering, this causes impurity occlusions, with potential for short-cutting, if mixing is not well monitored.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	H																
2	Li	Be											B 0.8	C 0.05	N 7×10^{-4}	O 0.25-1.25	F
3	Na	Mg 3.2×10^{-6}											Al 0.03	Si	P 0.35	S	Cl
4	K	Ca	Sc	Ti 2.0×10^{-6}	V 4×10^{-6}	Cr 1.1×10^{-5}	Mn 1.3×10^{-5}	Fe 6.4×10^{-4}	Co 2×10^{-5}	Ni 1.3×10^{-4}	Cu 8.0×10^{-4}	Zn $<1.0 \times 10^{-5}$	Ga 8×10^{-3}	Ge	As 0.3	Se	Br
5	Rb	Sr	Y	Zr $<1.7 \times 10^{-8}$	Nb $<4.4 \times 10^{-7}$	Mo 4.5×10^{-8}	Tc	Ru	Rh	Pd 5×10^{-5}	Ag 1.7×10^{-5}	Cd	In	Sn 0.032	Sb	Te	I
6	Cs	Ba	La	Hf	Ta 2.1×10^{-8}	W 1.7×10^{-8}	Re	Os	Ir	Pt	Au 2.5×10^{-5}	Hg	Ti	Pb	Bi	Po	At

Table 2: Segregation coefficient at Si melting temperature (k0) [Hopkins]

Crystallisation segregation is an efficient way to reduce transition metals. On the other hand, it is not efficient against oxygen and substitutional impurities (Al, B, C, P, Sn, As,…), many of which are donors or acceptors. For this reason, and considering the electronic activity of these elements, wafer c-Si cell makers are usually most concerned with substitutional impurities.

3.2.2. Effect of diffusion and precipitation during Si wafer cooling

When c-Si wafer cools down, the solid solution of impurity may precipitate due to the reduced solubility. The precipitation may also "freeze" at a given temperature, due to the reduced diffusivity.

Such precipitation of impurities (rather than the formation of homogeneous solid solutions) is favorable to passivate impurities. [Indeed, for a given impurity concentration, and with Np the number of precipitates, MC-precipitate effective collision surface, σ, is proportional to $N_p^{2/3}$, and hence MC lifetime increases with $N_p^{-1/3}$.] In addition, impurities with high diffusivity can migrate toward grain boundaries or lattice defects where they can passivated or removed.

Diffusion is especially favorable for some transition metals, such as Ni or Cu. [Transition metals form MeSi2 precipitates (FeSi2, CoSi2, NiSi2,…), at the exception of Cu which forms Cu3Si precipitates.]

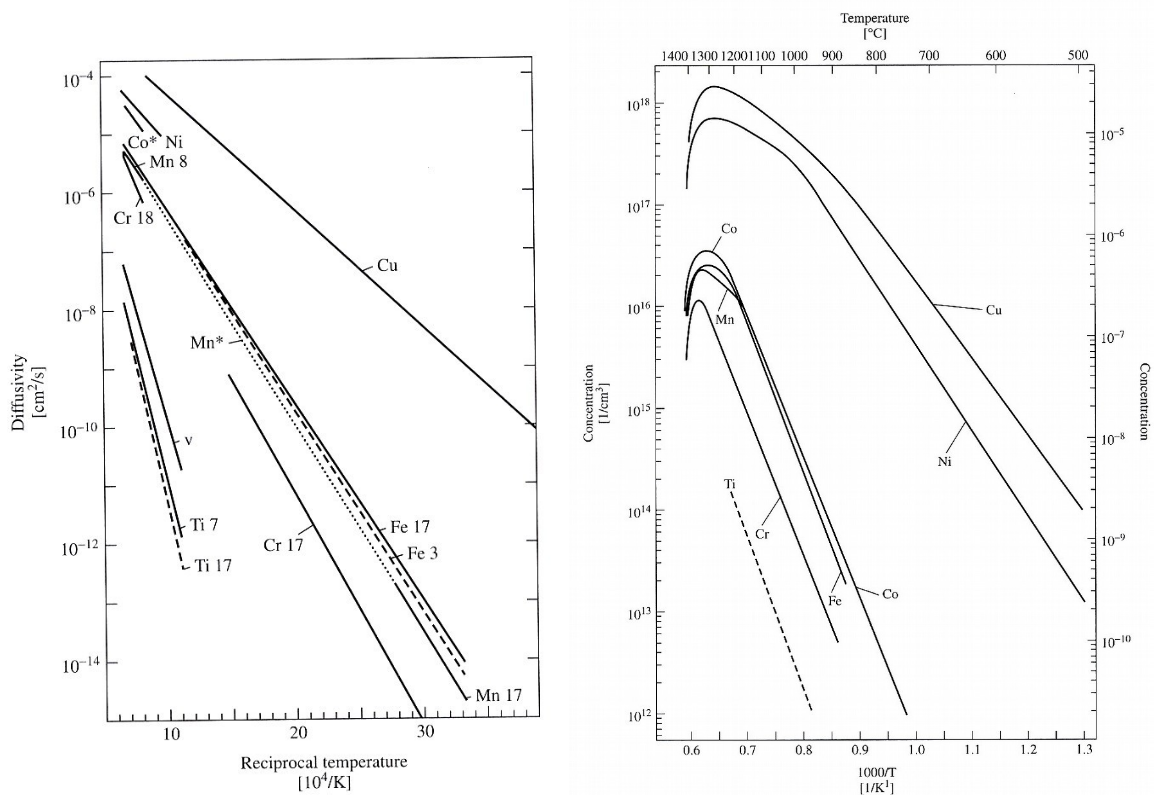

Fig 18: (left) Diffusivity of 3d transition metals as a function of the inverse sample temperature. [Metal impurities in silicon-device fabrication, p.29] (right) Solid solubility of 3d transition elements in silicon. [Handbook of photovoltaic science and engineering, p.191]

Notes: At crystallization temperature, the concentration of impurities is limited by their solubility in Si. For instance, transition metals have solubilibies in the 5.10^{13} - 5. 10^{15} at/cm^3 range. The impurity solubility at melting point is empirically found equal to 5.2 10^{21} k0 at/cm^3, with deviation for N, C, and O [Handbook of photovoltaic science and eng.].

3.2.3. Phosphorus doping and its gettering effect

P is the typical donor for the n-doping of wafer based c-Si cells. P (typically from POCl3) is deposited as a thin layer on the Si wafer, and diffuses to a limited depth.

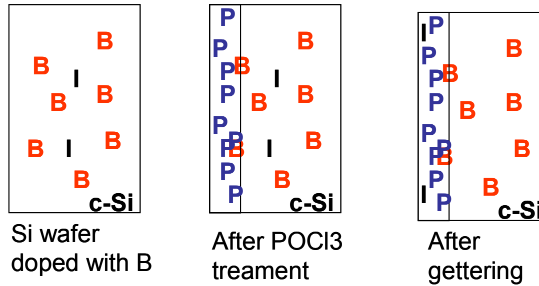

Fig. 19: POCl3 deposition on wafer and the following gettering step

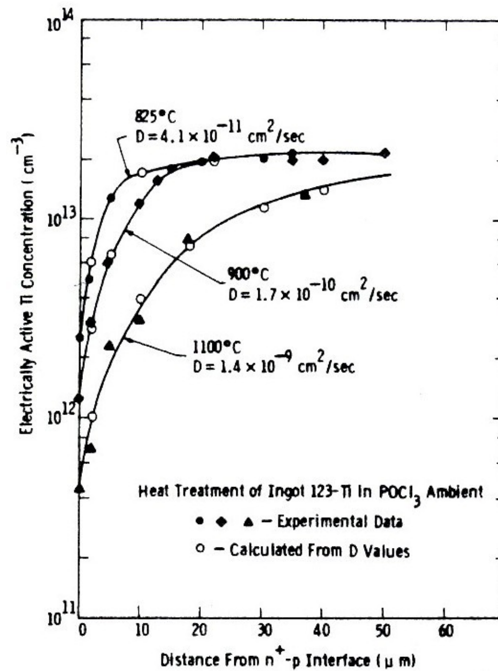

Fig. 20 Profiles of electrically-active Ti following 50 min POCl3 gettering. [Hopkins]

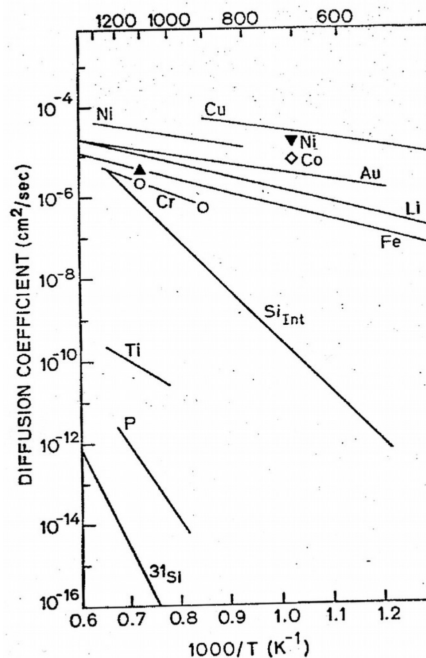

Fig. 21: Diffusivity of interstitial versus substitutional impurities [Dunham]

As a co-effect, on annealing, phosphorus removes impurities from the PV active zone ("gettering" effect). Impurities are attracted toward the surface (where they may be etched). This effect is especially important for multi-crystalline cells, in which metal impurities concentration can be close to the tolerance-level.

Although, the gettering effect is not fully understood, it is usually explained as follows:

- Metals are sunk by the phosphorus-rich zone because they have affinity for the lattice defects induced by phosphorus atoms. Metals have much higher diffusivity than phosphorus or boron, because they are interstitials and not substitutional in the Si lattice.
- Some metal atoms which are substitutionals, and hence do not diffuse well, can still diffuse if some interstitial Si atoms (which diffuse well) replace them in the lattice. It is thought that phosphorus treatment increases the concentration of interstitial Si in the wafer.
- Even if not etched and used in a junction, the phosphorus-doped zone being PV-inactive, its intrinsic tolerance to impurity is high.

3.2.4. Purity requirements for the silicon feed of wafer based Si cells

High grade silicon used in Si wafer manufacturing is obtained by the purification of a gas precursor (see annex). Here, we are concerned with the purity requirements at this level.

For metal purities, although the theoretical cell purity requirement in the cell is as low as 10 ppt, the actual metal purity requirement on the silicon feed is not that severe, mostly thanks to the natural segregation that occurs during wafer crystallization (see above).

On the other hand, substitutional impurities which are not well segregated by crystallization should be avoided in the silicon feed, especially those with donor or acceptor properties that are likely to influence the main doping (for instance P or Al, in a boron doped wafer).

Considering that these impurities should not perturbate the main doping, which is typically 1 ppm in the PV active zone, a global purity (determined by the most critical impurity) of the silicon feed below the 10 ppb level seems sufficient for the needs of PV-wafer makers.

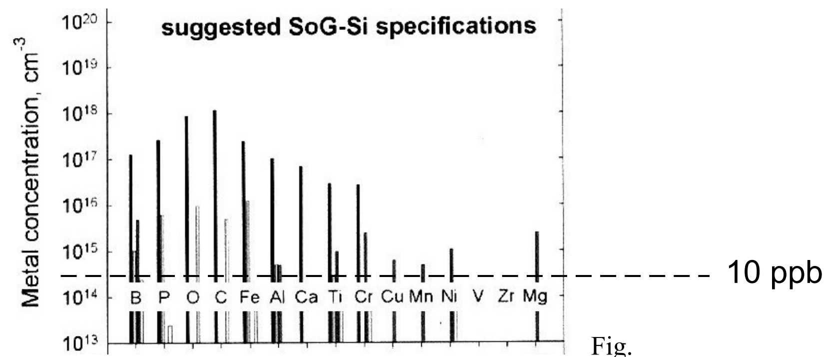

Fig. 22: Suggested silicon specifications for crystalline solar cells (several opinions from cell makers) [Istratov]

Note: Less pure silicon is not cheaper silicon! Considering that high grade (HG) silicon is somehow "too pure" for the PV applications, especially for some elements, many studies have explored the possibility of reducing production cost with less pure silicon source. However, today these researches have not proven successful. Indeed, most of the cost to make HG-Si is capital-cost and heat consumption (100kWh/ kg of Si) for the return trip to a purification-able gas phase (see annex). Hence, this cost does not depend on purity. In addition, a non-gaseous purification process of the cheap metallurgical grade (MG) silicon have not proven cost effective today due to the high number of steps that is necessary to treat each impurity.

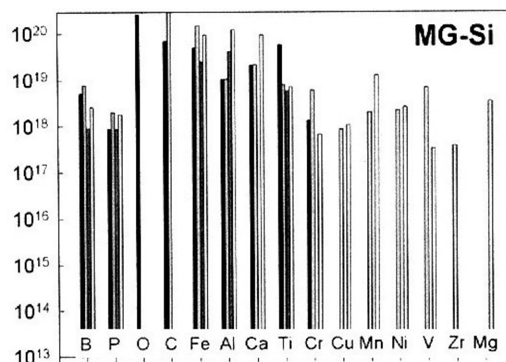

Fig. 23: Typical Metallurgical Grade Si purity [Istratov]

3.2.5. Purity requirement for wafer treatment gases, example of POCl3

Any chemical that it deposited on the Si wafer can potentially bring in its own impurities, and incorporate them into the PV active silicon (close to the junction). It is important to know the purity requirements for this gas feed.

For instance, during a POCl3 treatment, a layer of phophorus is deposited on the wafer. Both phosphorus and imported impurities penetrate the wafer as interstitials, but most impurities having higher diffusivity than phosphorus-interstitials (assumed close to that of Si interstitials, see figure 21) can potentially reach the PV active zone. (On further thermal annealing, phosphorus incorporates in the Si lattice, and becomes substitutional.)

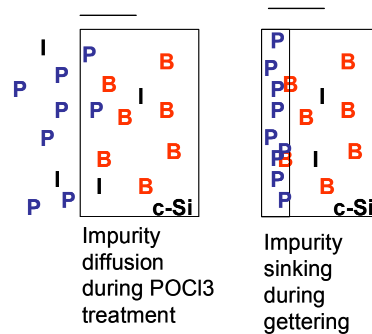

Fig. 24: Impurity contamination from POCl3 treatment

Roughly speaking the purity requirement for the depositing the gas is: X / (B x C), where, X is the purity requirement within the wafer (10 ppt to several %), B is the rate of impurity deposition relative to phosphorus deposition, C is the rate of impurity inclusion in Si (gettering effect included).

Considering that the deposition rate of some impurities can be as high as, or higher than, phosphorus deposition rate (oxygen in particular), and that gettering efficiency is limited (for instance gettering efficiency was measured 1 to 10^{-2} for iron [D. MacDonald]), we conclude that, as a rule of the thumb, the purity of the gas feed should be comparable to that of silicon for safe process.

Similarly, we could consider the deposition of an aluminium precursor, for Al doping, or for Al2O3 deposition. However, cell tolerance may be higher because Al is deposited away from the PV active zone (back side of the cell).

3.3. Purity requirements for thin film Si cells

3.3.1. Impurity tolerance within the cell

In a-Si, Si dangling bounds result in a continuum of energy levels within the band gap, with affinities for either electrons or holes (with two peaks at 0.04 eV from valence and conductive bands, see figure). These dangling bounds are very detrimental to carrier transport. They can act as temporary traps, as recombination centers, or as donor/acceptors.

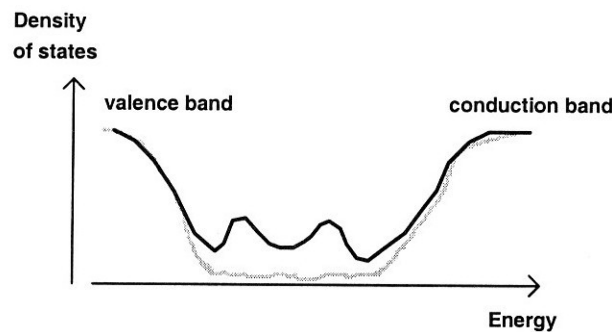

Fig. 25: Schematic of density of states before (black) and after (grey) passivation in amorphous silicon. Unpassivated dangling bond defects are responsible for peaks in the density of states deep in the band gap. Before passivation the defect density is so high that the material cannot be doped [The physics of solar cells].

Unpassivated a-Si has a defect density over $10^{16}/cm^3$ (20 ppb) and is not usable as a PV material due to the short carrier diffusion length. To reach carrier transport properties compatible with a PV cell, these dangling bounds must be passivated, and this is done with hydrogen. After passivation with H2 5-10%at, defect density is typically reduced to $10^{15}/cm^3$ (2 ppb).

The typical carrier lifetime in intrinsic a-Si:H reach 10-20 µs (for both carriers), and electron diffusion length reaches 0.1 µm [the physics of solar cells] (electron mobility is actually better than that of holes). This is sufficient for an intrinsic layer thickness of 0.3 µm, thanks to the electric drift induced by the p-i-n junction.

Comparing with c-Si, we note that:

- Carrier diffusion length in a-Si:H is 3 orders lower than the worst acceptable value in c-Si (100 µm considering optical absorption), however, this corresponds to a reduction of the diffusion coefficient, D (= a reduction of carrier mobility), rather than to a reduction of carrier lifetime. In fact, the a-Si:H, carrier lifetime (10-20 µs) is comparable to that of the worst acceptable (= critical) lifetimes in c-Si cells (say 10 µs). This indicates that, in a-Si:H, dangling bounds are active traps for carriers, but mild recombination centers.

- Electric conductivity in the intrinsic a-Si:H layer depends on the concentration of the remaining un-passivated Si dangling bounds, which are necessary to provide (both) charge carriers. As a result, PV efficiency strongly depends on H2 passivation, and hence is not well monitored.

- Impurities in a-Si:H cells may not only reduce carrier diffusion length, but also reduce the drifting effect, by charge perturbation in the junction.

For any form of silicon, lifetime can be expressed as: $1/\tau = 1/\tau_{Si} + 1/\tau_{impurity}$, τ_{Si} being the lifetime in the bulk Si (doping included), and $\tau_{impurity}$ being the lifetime considering only the collisions on the impurities. By cell design τ_{Si} is set over (or close) to the critical lifetime of the cell (typically 10 µs for both a-Si and c-Si). $\tau_{impurity}$ should also be over this value in order not to reduce cell performance.

$\tau_{impurity}$ only depends on impurity concentration and on the effective collision-section between impurities and charge carriers. $\tau_{impurity}$ almost does not depend on cell crystallinity (strictly speaking, it does a little through the electron/hole ratio). We conclude that the tolerance to active impurities within the cell is similar in a-Si:H cells and wafer-based c-Si cells.

We expect a similar tolerance to impurities for other types of silicon cells as well. Transport properties of micro-crystalline junctions are expected close that of a-Si-H. Transport properties of low temperature polycrystalline cells are expected close to that of wafer based c-Si cells.

Note: There is no obvious reason for such similarity, critical lifetime being set by design, which is itself based on the optical absorption properties of the material.

3.3.2. Silane purity requirement for CVD

Although the tolerance to active impurities is similar within a-Si:H cells and wafer-based c-Si cells, the purification and passivation mechanisms occurring during silane deposition at low T are different from that of wafer manufacture. This determines the actual gas feed requirements.

In low temperature deposition, there is no segregation by crystallization or by POCl3 gettering such as in wafer manufacturing, however there are similar mechanisms to consider, in particular:

- Elemental segregation in the gas phase (rate of deposition for the impurity).
- Passivation by a-Si dangling bounds
- Passivation by hydrogen.

Process-induced contaminations during gas deposition are also different from that of wafer manufacture. For instance the amount of metals (Fe, Ni,..) contamination is lower thanks to less metal

diffusion/evaporation (lower temperature). On the other hand, atmospheric contamination (oxygen and nitrogen) is expected higher, due to the large surfaces being processed.

Few studies are available for CVD deposition, which is unsurprising considering that silane feed is available in high grade from electronic market. Following are the results of two independent studies.

Study 1: tolerance to Oxygen and Nitrogen in PECVD (2008) [Woerdenweber]

Cell tolerance to oxygen and nitrogen contamination, and corresponding gas feed flow was measured (table 3). Cell tolerance is estimated at the onset of efficiency degradation (Fig. 26). However, the decrease of performance extends on a large range of impurity concentrations. Half-efficiency is obtained about 2 orders of concentration over onset concentration.

	Requirement in the cell	Corresponding partial pressure	Corresponding specification for SiH4	Corresponding specification for H2	Deposition speed to SiH4
Oxygen	$2x10^{19}$ at/cm3 (400 ppm)	$6x10^{-6}$ torr	28 ppm	0.6 ppm	7
Nitrogen	$4x10^{18}$ at/cm3 (80 ppm)	10^{-5} torr	47 ppm	1 ppm	0.85

Table 3: O and N tolerance for a-Si:H cells based on [Woerdenweber] Silane and hydrogen are deposited by PECVD with a silane/hydrogen molar ratio of 7.8/360 and a total pressure of 10 torr.

In this reference, it is mentioned that similar tolerance levels were obtained μc-Si cells obtained at high silane dilution in H2 (unpublished results).

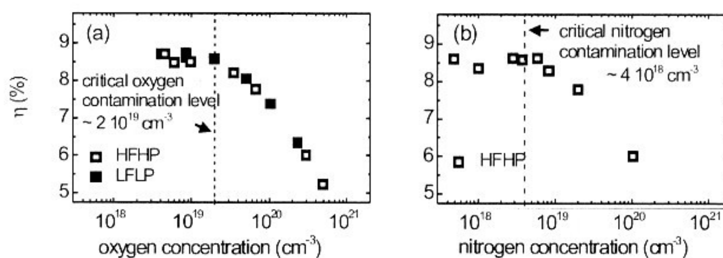

Fig. 26: Cell efficiency of the p-i-n a-Si:H solar cells versus impurity concentration in the i-layer, varied by oxygen and nitrogen flows in the deposition chamber. For oxygen two different deposition regimes are applied. [Woerdenweber]

Study 2: Tolerance to several common gases [DE Carlson and CR Wronski]

This older data was obtained for Schottky-barrier a-Si:H/Pt cells (table 4). The value for oxygen tolerance within the cell (3700ppm) is comparable to previous value (400 ppm) if considered that this value is not measured at onset, but after a 97% loss of efficiency. The value for nitrogen tolerance within the cell (8000 ppm) is a little high compared to previous reference (80 ppm), even if considered that this is measured after a 15% loss of efficiency. The deposition rate of N2 is also 5 times lower.

impurity	feed gas	partial vol (%)	Voc (mV)	Jsc (mA cm-2)	Fill Factor	efficiency ratio to ref	atomic ratio to Si in the cell in %	atomic ratio to Si in the cell in ppm	Deposition speed to Si feed	Note
none	SiH4	80	700	6	0.54	1	80	800000	1.00	
O	H2O	2.3	400	0.6	0.23	0.02433862	3.7	37000	1.61	
S	H2S	2.3	425	3	0.21	0.11805556				
Ge	GeH4	1	370	3	0.27	0.13214286	2.5	25000	2.50	
C	CH4	10	662	4	0.53	0.61880071	7	70000	0.70	below perturbation level
C	CH4	30	230	0.02	0.18	0.00036508	21	210000	0.70	
N	N2	10	595	6	0.55	0.86574074	0.8	8000	0.04	below perturbation level
P	PH3	0.06	130	1.5	0.42	0.03611111	0.04	400	0.67	
Cl	SiH2Cl2	50	321	0.05	0.25	0.00176918	7	70000	0.11	no SiH4

Table 4: Effect of impurities on the photovoltaic properties of a-Si:H solar cells [DE Carlson and CR Wronski] grown by several types of glow discharge CVD.

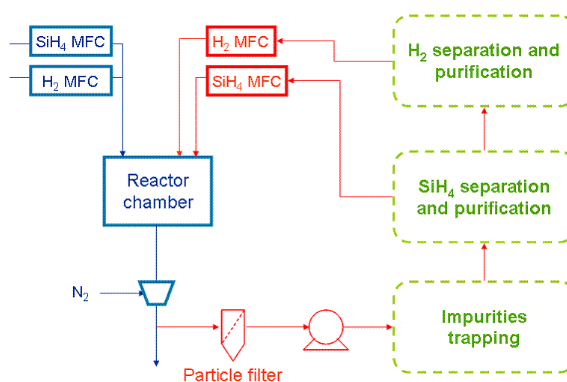

Fig. 27: Silane recycling project for thin films cell [Denis Jahan]. Oxygen and nitrogen purity request from customer was 1 ppm.

No tolerance data was found for low-temperature polycrystalline Si (a-Si deposited by CVD + rebaking at 600C). In this case, passivation-levels may be different due to the H2 being outgased when rebaking.

4. Conclusions

We have seen that the tolerance to impurity firstly depends on the impurity's electrical affinity for charge carriers, and more specifically to its capacity to reduce MC diffusion length. Most active impurities (lifetime killers) are transition metals for which the electronic tolerance level is theoretically as low as 10 ppt. Acceptor and donors (doping impurities) are also detrimental because they induce a perturbation to the main doping, and because they are readily incorporated in silicon as substitutional elements. Their level is typically required lower than 10 ppb.

However, we have seen that the PV cell can profit of various impurity passivation effects, including chemical passivation by hydrogen, oxygen, carbon or other co-impurities, or passivation by a-Si

dangling bounds. We have also seen that impurities can be removed or de-activated by thermal diffusion and precipitation, or by more complex gettering techniques.

Due to the variety of these effects, the purity requirement on the gas feed varies greatly from process to process and from impurity to impurity. Also, for a number of contaminants (O, C, Fe, Ni, N,…), contamination from gas feed is low compared to process contamination (from contacts, evaporation in the reactor, liquid treatments, atmospheric pollution,...).

For c-Si cells, the natural segregation of transition metal impurities during crystal growths greatly lowers the purity requirement on metals. For a-Si, such mechanism does not exist, however other mechanisms exist, such as gas phase segregation and hydrogen passivation.

All in all, the purity requirements for the gas sources are far milder the theorical 10ppt level. Practically, a carrier lifetime of 10µs in the PV active silicon can be considered as a minimum for all silicon cells.

Most severe purity Requirements		Transition metals (lifetime killers)	Donors / acceptors	Neutrals
Wafer c-Si	Tolerance to active impurities in the cell	10 ppt	10 ppb (main dopant: 1ppm)	100 ppm to several %
	Passivation	variable: diffusion (Cu, Ni), precipitation, gettering, chemical passivation (Fe)	variable	variable
	Tolerance to total impurities in the cell	10 ppt (Fe, Ni, Cu: 10 ppb)	10 ppb	100 ppm to several %
	Segregation (during crystallisation)	high (coef 10^-5 to 10^ - 8 for most active elements)	not much (coef 1 to 10^-2)	not much (C and Sn: coef around 10^-2)
	Tolerance at pre-wafering level	around the ppm	around 100 ppb	1000 ppm to several %
CVD deposited	Tolerance to active impurities in the cell	10 ppt	10 ppb (in intrinsic Si)	100 ppm to several %
	Passivation	high (hydrogen and dangling bound passivation)	high (hydrogen and dangling bound passivation)	variable
	Tolerance to total impurities in the cell	probably more than 1 ppb	ppm range (O: 400ppm, N: 80 ppm)	100 ppm to several %
	Segregation (during deposition)	very high as long as no metal particle is carried to the reactor	coef 10^-2 to 10 (oxygen segregation is negative)	not much
	Total (gas feed requirement)	excellent filtration of metal particles is needed	ppm range (in silane, O2: 30ppm, N2: 50ppm)	100 ppm to several %

Table 5: General summary (rule of the thumb): Tendencies in purity requirements for wafer based c-si cells, and CVD deposited Si cells.

ANNEX: SILICON PRODUCTION

Note: Silicon precursors melting points: SiH4 = -112C, SiH2Cl2 = 8.6C, SiHCl3 = 31.8C, SiCl = 57.6C

Silicon compounds are obtained from metallurgical grade Si (MG Si), which is obtained by thermo-reduction of the oxide: $SiO_2 + 2C \Rightarrow Si + 2CO$.

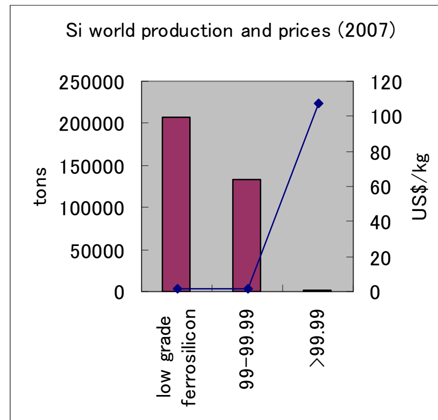

Fig. 27 Silicon world production (bars) and prices (line) in 2007 [US Geological survey commodity summaries]

To obtain high grade (HG) silicon there are mostly two processes, a traditional process (Siemens process, 60% of the market), that is being progressively replaced by a more recent process (Union carbide process). In both cases, MG Si is transformed to a gas/volatile compound for purification (fractional distillation), which is then decomposed back to silicon, but whereas the Siemens process purifies $SiHCl_3$, the UC process purifies SiH_4.

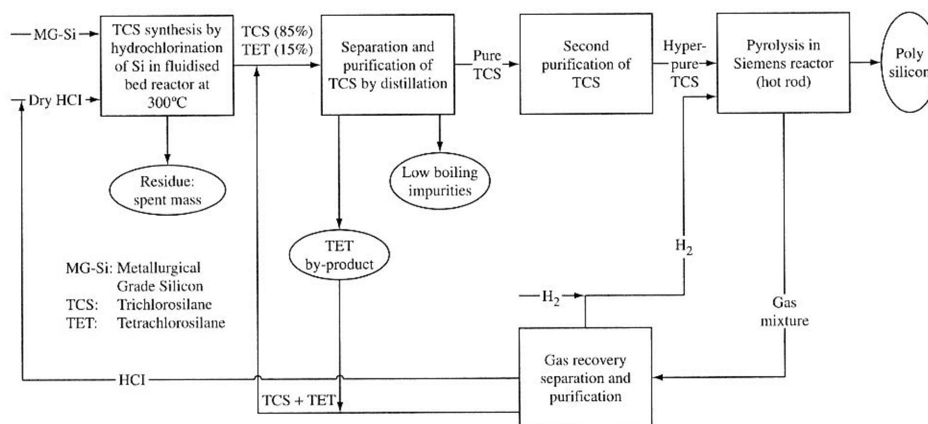

Fig. 28: Siemens process [Handbook of photovoltaic science and engineering]

- (to gas) $Si (MG) + 3HCl \Rightarrow SiHCl_3 + H_2 + SiCl_4$ (10-20%) [350C, no catalyst]
- (from gas) $3SiHCl_3 + H_2 \Rightarrow SiCl_4 + 2Si (HG) + 5HCl$ [1150C]

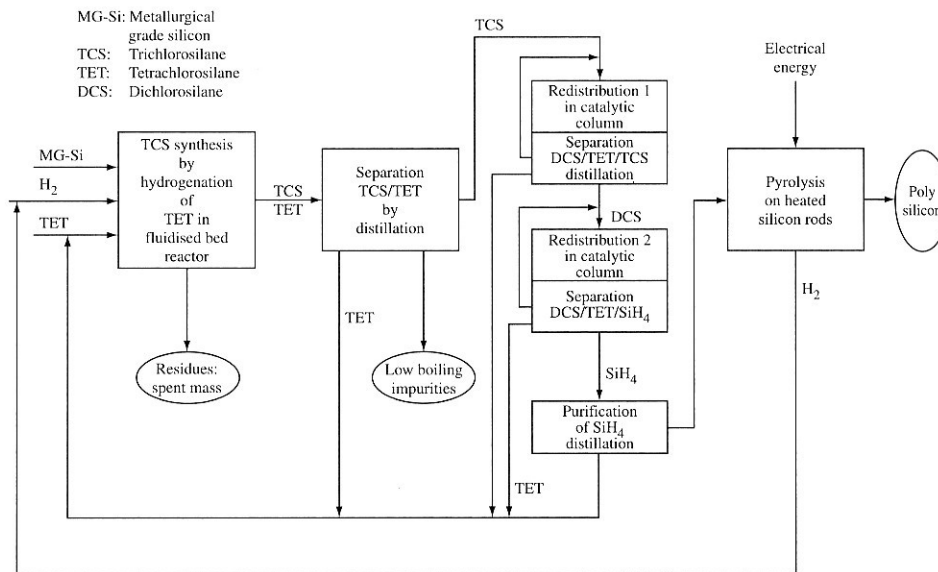

Fig. 28: *Union Carbide process (Technology acquired by REC)* [Handbook of photovoltaic science and engineering]

- *Si (MG) + 2H2 + 3SiCl4 (recycled) => 4SiHCl3 [500C, 35atm, with copper]*
- *SiHCl3 =catalyst> SiH2Cl2 + SiHCl3 + SiCl4*
- *SiH2Cl2 =catalyst> SiH4+ SiH2Cl2 + SiHCl3 + SiCl4*
- *Decomposition: SiH4 => Si (HG) + 2H2*

(first 3 reactions being followed by fractional distillation)

The UC process being chemically closed, there is almost no chemical input apart from MG Si (only minor H2 and SiCl4 losses must be compensated). On the other hand, the Siemens process is not chemically closed, and therefore has historically caused a SiCl4 surplus.

Note: The business model of AL-Denal, as established in the 90's, is to purchase SiCl4 and convert with the following reactions (followed by fractional distillation):

- *SiCl4 + H2 => SiHCl3 + HCl [1000C]*
- *SiHCl3 + H2 =catalytic> SiH4 (several steps)*

Today, it could more effective to recycle SiCl4 by the first reaction of the UC process.

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