

From electronic grade to solar grade silicon: chances and challenges in photovoltaics

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Dedicated to Professor Horst P. Strunk on the occasion of his 65th birthday

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Photovoltaics is a promising but challenging opportunity for the environmentally clean production of electric energy, as the cost of the produced energy is still too high to compete with conventional thermal and nuclear sources, in spite of the scientific and technological progress occurred in this field after the first oil crisis of 1973. Among the problems which should be solved to make photovoltaics fully competitive, a breakthrough concerning the cost reduction of the base material is compulsory. Aim of this paper is to discuss the scientific and technological problems encountered in the development of solar silicon for its use in high efficiency and low cost solar cells, and to give some firm experimental evidences about its potentialities.

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1 Introduction

Late in the seventies, silicon consolidated its key position in the field of terrestrial solar cells, leaving to GaAs the primate for space applications. The situation did not change significantly in the last two decades. In fact, see Fig. 1, silicon covers now, as single crystal, polycrystalline (wafers, ribbon and thin films) and amorphous almost the 100% of the photovoltaic production.

Still, in spite of a number of intrinsic advantages, such as its chemical stability, its environmental friendship, its large potential conversion efficiency ($\approx 29\%$) and the relative ease of processing, its high cost/area (from 200 to 500 \$/m²) and the huge production energy request (ca 300 kWh/kg using the conventional Siemens C process followed by the Czochralski (Cz) type of growth) was and is the critical drawback of crystalline silicon.

The high areal costs of crystalline silicon modules comes today at least in part ($\approx 30\%$) from the cost of the Cz-grown silicon ingots and wafers, prepared using electronic grade (EG) silicon. In fact, differently from microelectronic applications, where device size shrinkage makes the unit cost/device of electronic grade silicon almost unimportant at the submicron or nanoscale range, photovoltaics require large semiconductor areas to be employed and processed. At the today efficiency of the commercial modules (ca. 10%), a 10 kW plant requires 110 m² of modules.

For this reason, worldwide research efforts were spent in the last two decades, dedicated to the study

- a) of low cost processes for the production of multicrystalline or polycrystalline silicon wafers and ribbons, alternative to the Cz process for the growth of crystalline silicon ingots,
- b) of low cost processes for the production of polycrystalline silicon feedstocks using the gas phase route, and

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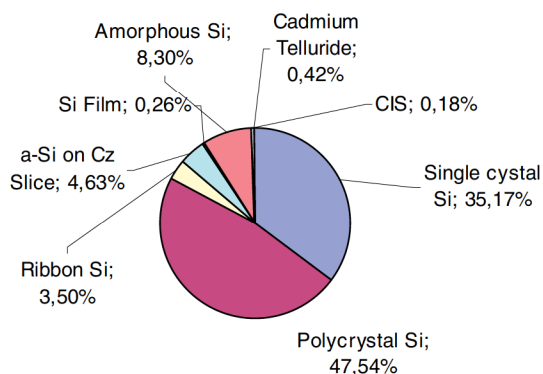


Fig. 1 (online colour at: www.pss-a.com) Present market distribution of silicon and non-silicon solar cells (CIS = CuInSe₂).

c) of a kind of a low-grade silicon, called solar grade silicon, which could be adapted to solar cell fabrication, without losing conversion efficiency.

The processes under a) were aimed at the production of crystalline, non-single crystal ingots, wafers and sheet and were developed under the hypothesis that casting processes are intrinsically lower in cost than the Czochralski one. The potential development of die molding processes for ribbon silicon growth looked even more advantageous. The penalty to be paid in this case is associated to the presence of grain boundaries and other structural defects in the material and to unavoidable contaminations due to the casting crucible and die materials.

The processes under b) were and are based on the development of low cost variants of the Siemens C route, which, as it is well known, is based on the energy intensive, high temperature reduction of purified chlorosilanes to polycrystalline silicon. Recent studies carried under the auspices of the European Commission within the fifth Framework Program showed that this route hardly could succeed in getting a polycrystalline feedstock at less than 25 €/kg, against the actual price of 90 \$/kg of that produced following the original Siemens route.

Very complex looked [1] and still looks the solution of problems associated to the production of a low grade silicon using variants of the metallurgical (MG) silicon process, with the aim to find alternative routes for the production of a low cost, low energy intensive polycrystalline feedstock. It was, in fact, figured that any material based on this processes would contain a quite large amount of impurities and structural defects.

Therefore, intense basic research studies were spent worldwide, with the objective of investigating the role of impurities and crystal defects on the minority carrier lifetime and minority and majority carriers mobility and to discover/develop remedies in their presence.

It is well known that the work carried out in the late seventies and in the early eighties, in spite of the impressive amount of knowledge achieved, did not succeed in the industrialization of one or even more new processes for low cost or solar grade silicon feedstocks.

The main reason of this lack of success was the limited size of the solar silicon market, which amounted to few MW of solar cells worldwide, the huge investment costs and the availability of several thousands of tons of EG silicon scraps, largely sufficient in amount and quality for their use as feedstock for the silicon casting processes.

Furthermore, the MG silicon route was considered impracticable, as will be shown in details later one, due to the unsolved problems relative to the removal of boron and phosphorous, present in more than ppm amounts in the best materials prepared following this route. Instead, the research work carried out in Germany, USA, France and Italy on the aim of developing a growth process which could be used in full alternative to the Cz process went to a successful development of a number of silicon casting and silicon ribbon production processes, which are still in use for the production of the multicrystalline silicon solar cells.

It is however quite remarkable that one of the gas-phase processes, delivering granular silicon is now in full industrial production of a polycrystalline silicon feedstock used in the Cz process, and that most of processes studied in the eighties, including the metallurgical silicon route, are now of actual interest for solar grade silicon, some of which in a phase of pre-industrialization, as a consequence of the large, overall increase of the PV market which occurred in the last ten years.

Furthermore, most of the research activity dedicated to the study of the electrical properties of deep level impurities, point defects, extended defects, and to the study of impurity/defect gettering and passivation processes, entered in the main stream of those basic studies which are now of main interest for the development of state of the art EG silicon, Si-Ge and nanocrystalline silicon devices.

Aim of the present paper is to analyse some of the basic physico-chemical problems which should be considered and solved when using multicrystalline, polycrystalline or nanocrystalline substrates for high efficiency solar cells, leaving out of consideration those encountered in the solar cell design and fabrication, making systematic reference to the studies which were performed in the years in our laboratory. It will be shown that a major role is played by chemical interactions between impurities and structural defects and that, therefore, chemistry should be used to manage the problems associated with defective and impure semiconductors for PV (and optoelectronic) applications.

2 Crystalline vs polycrystalline solar cells: generalities

As it is well known, Czochralski silicon is a mature material, whose physical and chemical properties were and are specifically modelled for microelectronic uses. Its preparation requires an ultra high quality polycrystalline feedstock, generally prepared using the Siemens C route. Its properties, in turn, depend on the amount of oxygen and residual metallic impurities, on the crystal imperfection (mainly dislocations) and on the amount of point defects (vacancies and interstitials). Its high quality does allow the fabrication of highly efficient solar cells, reaching now figures close to the theoretical limit, but its high cost and limited availability with respect to the potential market prevented and still prevent the achievement of a target cost of less than 1 €/Watt peak for terrestrial solar cells (The rated power, expressed in Watt peak, is a measure of how much energy a solar panel can produce under optimal conditions).

The ubiquitous presence of grain boundaries (GB) in poly/microcrystalline silicon thin film sheets, on the other side, prevented their use in photovoltaics, as the presence of GBs degrades the minority carrier lifetime to unacceptably low values.

From the huge amount of papers which have been dedicated to the study of the electrical properties of grain boundaries (GBs) and dislocations in semiconductor materials [2–6] it comes out, however, that in large grained material GBs become a tolerable structural defect.

2.1 Multicrystalline silicon

Large grained and columnar polycrystalline silicon, conventionally named multicrystalline (mc)silicon, was found to be a relatively low cost alternative to Cz, in spite of the presence of GBs. Large columnar grains minimize carrier recombination and mobility losses, provided their orientation is parallel to the drift and diffusion paths of carriers to the junction and the base contact, thus minimizing the GB influence on the final efficiency of the solar cells.

In fact, terrestrial modules with efficiencies close to 20% are now currently manufactured using multicrystalline silicon.

This material is generally prepared with variants of the directional solidification (DS) technique, whose basic features are the high throughput and the relaxed energy consumption costs (≈ 8 kWhr/kg vs. 60 kWhr/kg for the Cz process). Its extensive application went possible with the discovery that graphite, originally used by Wacker Heliotronic for its casting process [7], could be substituted by a quartz crucible lined with silicon nitride, which prevents the wetting of quartz walls by liquid silicon and the consequent destructive stress at the quartz/silicon interface after solidification [8].

The use of quartz crucibles is however the ultimate drawback of the technique, as it will limit the achievable size of the ingots.

Among the advantages of the DS technique, it should be mentioned that it allows the growth of oriented grains and prevents the carbon contamination by a graphite crucible, avoiding one of the main drawbacks of the original Wacker casting process. Carbon supersaturation causes, in fact, the precipitation of SiC which is a powerful source of minority carrier losses.

So far, DS feedstocks originate from the several thousands of tons of Cz silicon scraps (heads and bottoms of Cz ingots, discarded wafers, etc.) whose quality is appropriate for PV uses, as DS allows, if necessary, a substantial purification of the melt, confining the impurities in a narrow and well defined region on the top of the ingot. As in the Cz process, the effective segregation coefficients depends on the growth rate but there is an unavoidable segregation of impurities at grain boundaries, which is almost unimportant using EG feedstocks but severe in the case of low grade feedstocks, as it will be shown in this and in the next Sections.

Already in the eighties [9] it was, in fact, shown that the average values of the diffusion lengths in large grain DS silicon prepared with EG feedstocks compared with those of Cz silicon, reaching values close to 200 μm , and it was therefore emphasized that any improvement in the PV behaviour of large grained polycrystalline materials passes through the improvement of the intragrain properties (impurity content, dislocation density, precipitates), as the overall GB density is low and not all GBs are electrically active. The primary cause of reduced conversion efficiency was shown to be, in particular, due to regions of high minority carrier recombination, generally characterized by high dislocation density [10–12].

It is however recognized that *clean* dislocations should be electrically inactive at room temperature because of structural reconstruction [14] and that transition metals would introduce dislocation-associated deep levels [15].

2.2 Role of grain boundaries

It is also widely accepted that GBs introduce deep levels acting as recombination centres of minority carriers. These deep levels are attributed to intrinsic structural defects such as dangling bonds or extrinsic impurity contamination.

Seifert et al. [16] reported, in fact, that the recombination activity of GBs is related to the density of dislocations in/at the boundary and that impurity segregation produces an additional activity.

Chen et al. [17] eventually, have studied the effect of GB character (Σ values) and boundary planes on the electrical properties of GBs. They demonstrated that the recombination activity at room temperature of contamination-free GBs is weak and the GB structure has minor effect on the electrical GB properties. They also studied the impact of the impurity contamination on the recombination activity of grain

Table 1 Impurity distribution along a DS ingot grown from purified MG silicon (ingot dimension: $23 \times 23 \times 20 \text{ cm}^3$, slice thickness: 400 μm).

element	starting concentration (ppmw)	slice nr						
		19	21	23	50	52	54	top
Al	52	2.0	3.0	2.0	4.0	2.7	5.5	>1500
B	3.0	2.5	2.1	2.2	2.4	3.1	3.1	8.7
P	6.0	3.2	3.4	6.8	8.8	6.1	11	300
Ca	36	48	67	91	135	>150	>150	>1500
Mg	14	19	27	40	62	70	60	250
Fe	33	3.4	<1	<1	1.7	<1	2.0	>6000
Ti	32	<1	<1	<1	<1	<1	1.7	>1500

Table 2 Effective segregation coefficient of metallic impurities in DS grown multicrystalline silicon ingots from purified MG feedstock.

element	effective Cz	effective DS
Cu	6.9×10^{-4}	2.10^{-3}
Cr	1.1×10^{-5}	3.7×10^{-3}
Fe	6.4×10^{-6}	1.6×10^{-4}
Ni	3.2×10^{-5}	9×10^{-4}
Ti	3.6×10^{-6}	2.5×10^{-3}
Zr	1.5×10^{-8}	7.7×10^{-4}

boundaries in mc-silicon cut from different solidification positions of a B-doped ingot [18, 19]. The metallic impurities content in the samples studied, except for Fe, was under the detection limit. The Fe concentration was below $5 \times 10^{12} \text{ cm}^{-3}$ at the central position and was of the order of 10^{15} cm^{-3} at the top and bottom positions.

They showed that in the central and top (solidified last) sections of the mc-Si ingot, the recombination activity of GBs was weak at 300 K, whereas in the bottom (solidified first) section some GBs showed enhanced recombination activity, which was attributed to the effects of iron and additional impurity contamination. Our studies [20] about the segregation profile of impurities in DS ingots grown from a purified MG silicon feedstock showed instead (see as example Table 1) that most of the impurities collect on the very top of the ingot and that the effective segregation coefficients of impurities deviate systematically from those experimented in Cz growth, as it is shown in Table 2.

The difference is particularly sensible in the case of Ti and Zr, but important also in the case of iron.

These results show that the thermodynamics of segregation is influenced by the presence of extended defects (GBs and dislocations) which behave as heterogeneous nucleation centres for supersaturated impurities as well as gettering sites. The strong deviation relative to Zr and Ti, both very reactive with oxygen, indicates also a possible influence of dissolved oxygen on their effective segregation coefficient. We will discuss in details this topic in Section 6, devoted specifically to metallic impurities and to their interaction with extended defects and oxygen.

Our recent studies have shown also a different behaviour for both the recombination activity of GBs and the average diffusion length (L_d) in n-type materials. Figure 2 reports three Electron Beam Induced Current (EBIC) contrast maps obtained on the same GB of samples coming from different solidification position of the ingot but lying on the same columnar grain. Here the EBIC contrast is conventionally defined as $C = (I_b - I_g)/I_b$ where I_b and I_g are the EBIC currents in the bulk of the grain and at the GB, respectively. One can observe that in disagreement with the Chen results [17] the contrast takes its maximum value on the top and the minimum in the mid.

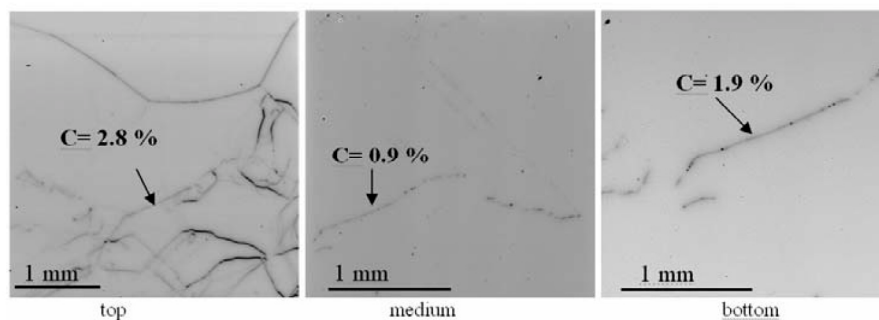


Fig. 2 EBIC contrast maps in correspondence of different sections of the same columnar grain. The contrast figures refer to the same GB.

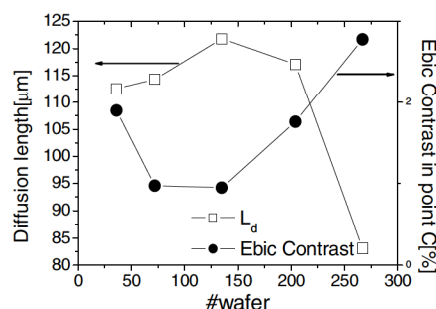


Fig. 3 EBIC contrast and diffusion length evolution along the solidification direction of a n-type mc-silicon ingot (the bottom region starts on the left).

If the contrast profile along the growth direction is compared with that of the bulk diffusion length, (see Fig. 3) one could remark that a good correlation exists between GB activity and diffusion length, both of which showing a strong degradation in correspondence of the top of the ingot.

As above mentioned, metallic impurities have a strong detrimental effect both on the local GBs properties and on the average diffusion length. Therefore, we could explain the data reported in Figs. 2 and 3 as an effect of a metallic impurity, possibly iron, which is a major contaminant of the silicon nitride liner of the quartz crucible and which is therefore expected to be dissolved in the Si matrix.

Since the bottom and lateral positions of the ingot face the crucible walls, iron would continue to diffuse into these regions during the ingot growth. At the end of crystal growth, the concentration of impurities in the silicon melt reaches its maximum value due to accumulated impurity segregation, leading therefore to the worse figures of both contrast and L_d , indicating that both the intragrain and the GB properties are degraded by the impurity contamination.

Therefore, the argument that the diffusion length and, consequently, the solar cell efficiency passes through the sole improvement of the intragrain properties, might not be applied straightforwardly neither to multicrystalline materials prepared from lower grade feedstocks, nor to those prepared from EG feedstocks, as the electrical activity of mc-Si is depending also on the thermal history of the sample investigated.

Considering first EG-based DS microcrystalline Si, its major contaminants are oxygen, carbon and, possibly, nitrogen, which are the native impurities of this kind of material. Although their effect will be considered in the appropriate Section, it should be mentioned here that they might influence the intragrain properties as well as the grain boundary properties [21].

In the case of non-EG grade feedstocks, metallic and non-metallic impurities, including boron and phosphorous, might be present in addition to the native impurities: depending on their amount, also these impurities might affect both GB and intragrain properties.

Finally, extended defects like dislocations and precipitated inclusions from supersaturated solutions of impurities are known to affect severely the electronic properties, and thus also the photovoltaic ones, of mc-Si. Dislocations might be partially or totally reconstructed, and is the amount of unsaturated bonds and of segregated impurities which rules their electrical activity.

About GBs, a wide literature exists dealing with their properties, which depend on the nature of each single GB and on its contamination. Each GB might be depicted as an internal surface, whose structural properties are affected by the specific reciprocal misorientation of the neighbouring grains and whose physico-chemical properties are ruled by the residual unsaturated (dangling) bonds and by other structural defects. High symmetry GBs might be entirely reconstructed and therefore electrically inactive, low symmetry GBs are instead only partially reconstructed and present both chemical and electrical activity. In the first case we expect only relatively shallow states associated to dilated or distorted bonds, in the second one deep gap states associated to unsaturated bonds.

Thermodynamics and chemistry are the responsible of GB reconstruction during growth or any subsequent high temperature treatment, and thus also during the solar cell fabrication processes. The extent

of reconstruction is that needed to minimize the excess Gibbs free energy due to presence of defects. Reconstruction in *clean* materials would imply only structural reconstruction. In the presence of impurities a kind of chemical reconstruction might play a major role, addressing at the impurity interaction with GBs, which also act as heterogeneous nucleation centres for supersaturated impurities. Chemical interaction with metallic impurities leads to silicide bond formation while interaction with non metallic-impurities (O, C, N) leads to more complex bond structures including oxide, carbide and nitride bonds. Depending on the bond formation energy, deep gap centres associated to unsaturated bonds might be removed from the gap and transformed in electrically inactive centres. These kinds of processes, of which the most known is that involving hydrogen, lead to the unsaturated bond passivation by impurity gettering and, possibly, to GB inactivation. As a consequence of impurity gettering at GBs, the formation of a impurity denuded zone occurs, whose depth depends on the diffusivity of any specific impurity and might approximated to its diffusion length $L_D = \sqrt{Dt}$, where D is the diffusion coefficient and t is the annealing time. This approximation holds uniquely if one could neglect the presence of GB strain fields, due to interface excess energy, which plays an additional role in the collection of the impurities. Multiple impurity gettering leads, therefore, not to unique depletion region (denuded zone in microelectronic sense).

Impurity gettering at extended defects has been recently modelled [22] in relationship to silicon microelectronic processes, but its features were experimentally studied since many years in relationship to multicrystalline materials [21], also allowing the development of specific extrinsic gettering processes [23]. We intend to briefly mention here only the key role played by point defects on the precipitation of supersaturated impurities at GBs, as well as that played by the stress fields induced by volume misfits.

As an example, it was shown that in the case of oxygen and carbon segregation, oxygen segregates in close correspondence with the geometrical position of the GB while carbon presents two satellite peaks spatially resolved from the oxygen peak [24]. This result is explained by assuming that the compressive strain field generated by SiO_x segregation at GB is compensated by the tensile field associated by C agglomeration or segregation, leading to local conditions of mechanical (hydrostatic) equilibrium, in good agreement with the exigent volume models of Tan [25] and Hu [26], which account for the different molar volumes of Si, SiC and SiO_2 , being $V_{\text{SiO}_2} \approx 2V_{\text{Si}}$; $V_{\text{SiC}} \approx 1/2 V_{\text{Si}}$. In carbon-free samples, instead, the strain field associated to oxygen segregation is released by dislocation emission, which are punched out by the precipitates when self-interstitials supersaturation conditions occur. Silicon self-interstitials (Si_i) are, in fact, reaction partners in the oxide phase formation, which can be formally written as



as their emission creates locally the volume needed to accomodate the oxide phase in the silicon matrix. Self-interstitials are, as well, the reaction partners in the SiC formation



As in solid state reactions or transformations full equilibrium conditions are satisfied only in the simultaneous presence of thermodynamic and mechanical equilibrium, of which the last implies the absence of local stresses, we might foresee the achievement of full equilibrium conditions when O and C co-segregate as spatially separate phases.

In addition, as could be inferred from simple thermodynamic considerations, every internal surface might behave as a phase of reduced dimensionality, with properties substantially different from the bulk phase, due to the different coordination and bonding of atoms in the low dimensionality phase. Grain boundaries should present such a behaviour and the impurity segregation at GB might be discussed as the impurity repartition between phases of unlike dimensionality, in the same way one discusses the equilibrium between condensed phases of different composition [27].

The physical and chemical properties of a poly-multi/crystalline material depend, therefore, in a very complex manner on the properties of both the GBs and the bulk of the grains, and are true local properties, as different equilibrium conditions arise in correspondence of specific grains or specific GBs.

However, they will depend only on their intragrain properties when segregation of impurities at GB from undersaturated solutions induces bond formation at unsaturated bonds and, then, GB passivation. Intragrain properties are quite inhomogeneous in this case, as one should have a region of a thickness approximately equal to $\sqrt{Dt}$ close to the GB which is depleted by impurities and a true bulk region. As the thickness of the denuded zone depends on the diffusion coefficient of impurities, one might assume that the intragrain “bulk” volume properties are dominated by the slow-diffusion impurities, like carbon, oxygen and nitrogen, as fast-diffusion impurities, like the metallic ones, should be easily gettered at GBs and their depletion region might extend to the entire volume of the grain.

Denuded zone effect has been recently demonstrated by Jingang Lu et al. [28] in nitrogen-rich silicon polycrystalline sheets. They showed that silicon oxynitride precipitates preferentially at GB, leaving a well defined denuded zone and that the intragrain defects consist of stacking faults, associated to oxide precipitates homogeneously nucleated.

When supersaturation conditions occur, extended defects behave as heterogeneous nucleation centres for second phase formation: in this case the GB properties depend on the electronic properties of the deposited phases, which, in turn, might be the nucleation centres of dislocations, if in their presence a stress/strain field sets-up.

Quite generally, therefore, one has to consider that the properties of polycrystalline/multicrystalline silicon are dominated by impurities, GBs and dislocations.

Studying the properties of *clean* GB seems to be, however, almost impossible, as GBs must be, for thermodynamic constraints, always contaminated by residual impurities. We will show in the next Section that this happens for GB contaminated with oxygen, but the same evidence has been given for dislocations, whose electrical activity was demonstrated to depend on gettered impurities [29].

The discussion of the electrical activity of GBs requires, therefore, a deep insight on the chemical contamination of the boundary, as will be shown in the next Sections.

3 Native impurities (oxygen, carbon, nitrogen) in microcrystalline silicon

It is well known that oxygen, carbon and nitrogen impurities in EG silicon were the subject of intense investigations in the last three decades, giving origin to about a million of papers devoted to oxygen, 1,6 million of papers devoted to carbon and to more than 700000 papers to nitrogen.

We intend here to discuss only their key influence on the physico-chemical properties of mc-silicon, mostly on the base of the work which has been carried out in our Laboratories until recently.

One of the main effects, already observed in our previous experiments and later one by Radzinski et al. [13] is the key role of oxygen and carbon, whose concentration depends on the growth conditions, on the electrical activity of GBs.

We have experimentally demonstrated that the concentration of dissolved oxygen (N_O) and carbon (N_C) in DS silicon is a quasi-equilibrium property, defined by the constant

$$K = N_O \times N_C, \quad (3)$$

which accounts also for the repartition coefficient of carbon and oxygen within the solid and liquid phase [12].

In our earlier samples their concentration varies continuously from the bottom to the top of the ingot, with values which range from 10 ppma O and 2.5 ppma C to 10 ppma of C and 2.5 ppma of oxygen.

This range of concentrations is also typical of commercial ingots nowadays, as it is shown in Fig. 4.

These studies allowed also the identification of a region where second phase formation occurs with the precipitation of an (oxi)-carbide phase. Precipitation, monitored by microstructural examinations, occurs when the carbon concentration is larger than 7 ppma and the oxygen concentration is lower than 2.5 ppma. As the oxygen content takes these critical values only in correspondence of the least fraction solidified (see Fig. 4), precipitates are confined on the top of the ingot. We have also shown that the diffusion length depends on the oxygen and carbon content and takes the largest values in correspon-

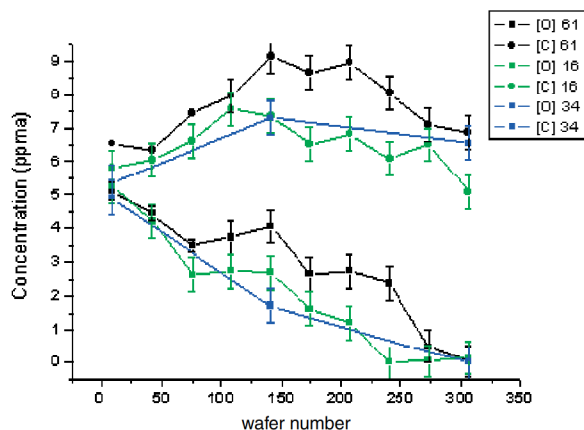


Fig. 4 (online colour at: www.pss-a.com) Oxygen and carbon concentration profiles in a n-type multicrystalline silicon ingot (the bottom region starts on the left).

dence of solid solutions containing equimolar concentrations of oxygen and carbon. This result is in quite good correlation with the achievement of mechanical equilibrium conditions due to a compensation of tensile and compressive fields associated to the segregation of these impurities (see reactions 1) and 2) and comments therein).

Intragrain precipitation of (oxi)carbides is generally anticipated or associated to the segregation of carbon and oxygen at GB, which can be detected using FTIR [31] and SIMS [32] measurements in GB scanning or mapping configuration. It is interesting to remark that FTIR measurements of the IR active interstitial oxygen concentration across a GB showed that oxygen segregates in close correspondence with the GB geometrical position already in the as grown material and that its relative concentration does not change significantly after an high temperature annealing.

It implies that the GBs are decorated by oxygen already in the as-grown state, with deep implications on their electronic structure.

These IR measurements are however specific for self-interstitial oxygen and do not monitor the oxygen associated to oxide precipitates, differently from SIMS measurements which detect the total oxygen (and carbon). The additional advantage of SIMS is to allow the detection of the segregation of oxygen and (or) carbon as the oxide or carbide phase by the simultaneous shift of the carbon, oxygen and silicon signals. In the case of our DS grown samples, SIMS measurements [24] allowed to put in clear evidence the segregation of both oxygen and carbon along grain boundaries, and infer that their spatially separated segregation occurs only when the carbide and oxide phases are present.

Equi-concentrated or almost equi-concentrated samples ($N_O - N_C \approx 0$) present the less active GBs (lower barrier height) with respect to samples where one of the two impurities prevail. On the base of the oxygen and carbon profiles shown in Fig. 4 these samples are confined to a small vertical section of the ingot, up to the half of it. As reported in the previous Section a low GB activity could be explained considering the different molar volume of the Si, SiC and SiO₂ species that could agglomerate or segregate to or near GBs.

Finally, it was also shown that the intragrain dislocation density depends on the oxygen excess or defect, with the almost total suppression of dislocations for ($N_O - N_C$) values close to zero [32].

These result reinforce our previous conclusion that mechanical equilibrium conditions rule the behaviour of carbon and oxygen impurities and suggest also their possible role on the electrical properties of multicrystalline silicon in the absence of metallic impurity contamination.

In good agreement with this hypothesis, it was demonstrated [12] that the sole carbon segregation at a GB invariably induces a strong recombination activity, while in oxygen rich or equiconcentrated samples [$(N_O - N_C) \approx 0$] the GBs are only slightly recombining and the average diffusion length takes its maximum value.

The behaviour of multicrystalline samples containing a slight excess of oxygen over carbon, carefully studied in function of the annealing temperature [33, 34], did allow a better understanding of the crucial role of oxygen. It was in fact observed that both the local bulk diffusion length and the GB contrast determined by means of Electron Beam Induced Current (EBIC) measurements show a strong decrease after a two step annealing at 450 °C and then at 650 °C. In addition, it was shown that the EBIC contrast presents a maximum at 650 °C while the diffusion length decreases monotonically with the increase of the annealing temperature. These results might be interpreted by considering that oxygen segregated at temperatures higher than 650 °C passivates GBs. Instead, the old-and new thermal donors, generated at 450 °C and 650 °C, respectively, degrade the diffusion length.

This conclusion is supported by local measurements of the electrical activity of GBs, carried out by electrical conductivity measurements, which demonstrated that not only the minority carrier properties, as shown above, but also the majority carriers ones are influenced by impurity contamination.

Trans-barrier dc conductivity measurements carried out on single GBs which were contaminated with carbon, oxygen and carbon showed [35], in fact, that only GBs decorated with carbon exhibit a temperature activated behaviour, while GBs decorated with oxygen display a behaviour which is comparable with that of single crystal silicon.

It could be concluded that the deep traps and gap states responsible of mobility drops and minority carrier recombination losses are associated to the segregation of native impurities and not to intrinsic surface states, in good support of our previous considerations about *clean* GB, that are intrinsically thermodynamically unstable objects.

It is quite interesting to consider that similar considerations were recently raised by us for the recombination activity of dislocations in EG silicon [36].

It could be therefore also concluded that multicrystalline silicon in which carbon-oxygen compensation occurs presents close similarities with crucible grown Cz silicon.

Very little is known, instead, about the role of nitrogen, whose concentration is high in the polycrystalline sheets studied by Radzimski et al. [13] and at the periphery of our polycrystalline silicon ingots. In the first case oxynitride precipitation at GB was observed by TEM. In our case [31], TEM and electron diffraction measurements on selected samples taken at the periphery of the ingots showed the presence also of silicon nitride and iron silicide (Fe_3Si_5) precipitates. These last were also shown to behave as nucleation centres for dislocations.

4 Dopant impurities (B, P, Al)

The knowledge of the threshold concentration of B and P as single or multiple impurities is of primary importance for the today employment of highly doped silicon feedstocks and of future “solar grade” feedstocks, as they represent, together with carbon, the least easily removable impurities from a MG silicon feedstocks. Based on the average content of boron in the quartz used in the MG silicon industry, a B concentration around 10 ppma (10^{18} cm^{-3}) is the expected figure, which would lead to a bulk resistivity value of about $0.01 \Omega \text{ cm}$, too low to get acceptable conversion efficiencies, which require, for single crystal EG silicon, an optimal bulk resistivity not less than $0.5 \Omega \text{ cm}$ [37]. Using solidification techniques its removal is impossible, as the segregation coefficient of boron is close to one and chemistry is apparently unable to remove boron from silicon melts via the formation of stable boron compounds.

The main advantage of the Siemens C process, on the other side, is the removal of boron, together with other volatile chlorides, from a gaseous chlorosilanes mixture. In spite of these heavy problems, limited attention has been paid on the effect of these impurities on the PV behaviour, although it is well known from the literature [38] that at even at dopant concentrations lower than 10^{18} cm^{-3} these shallow acceptor traps affect substantially the carrier lifetime.

One possible alternative to the Siemens C route could be the electrical compensation of boron with donors, like P or As, but the amount of possible compensation is still an unknown. Our studies [39] showed that the lifetime and the photovoltaic properties of p-type single crystal silicon are not appreciably affected by the contemporaneous presence of donors and acceptors, provided the *excess* acceptor

concentration is lower than 5×10^{16} at cm^{-3} . Above this threshold, the lifetime decreases and the relative normalized cell efficiency drops suddenly from values close to 1 to values close to 0.5. Apparently, the density of the electrostatically bonded B an P pairs is uninfluential on the minority properties, while the excess acceptor concentration dominates the same properties. The range of boron concentrations investigated is however too far from their concentrations in MG grade or heavily doped EG silicon feedstocks to consider these data useful. To our knowledge, however, compensation at larger B an P concentration has not been studied so far.

SIMS measurements succeeded instead to show that in the presence of carbon, boron segregates at GB. This event is signalled by an hundredfold increase of the B signal respect to the boron background of the sample [33]. This result can be interpreted as a good example of a segregation process dominated by a chemical reaction, considering that B–C complexes belong to the stable acceptor-X centres [40] series, with an ionization energy slightly lower than the unpaired acceptor. GBs could be therefore used to segregate B from the bulk, but the increase of their electrical activity should be investigated to judge the effectiveness of the process.

Additional measurements were also carried out on Al-doped polycrystalline samples [41], an acceptor impurity which is present in large amounts in MG feedstocks and which presents, like other dopant impurities, unfavourable segregation coefficients. It was shown that the hole mobility and the carrier concentration decreases for Al concentrations larger than 10^{17} cm^{-3} , while the diffusion length decreases monotonically already for Al contents larger than 10^{16} cm^{-3} . It was suggested, therefore, that part of the Al segregates at GB with their consequent passivation and that precipitation occurs in heavily concentrated ($>10^{19} \text{ cm}^{-3}$) samples, as observed by TEM measurements. The presence of two deep levels at 0.315 and 0.378 eV was finally detected by means of Deep Level Transient Spectroscopy (DLTS), of which the second is a hole trap and the first is a recombination centre, both possibly associated to the Al–O centres detected by Marchand and Shah in single crystal silicon [42].

5 Deep level impurities and a definition of solar silicon

The deep level impurity content in EG silicon dictates its capability to work not only as substrate for microelectronic devices but also as an efficient solar energy converter, as deep level impurities behave as minority carriers recombination centres.

With the last category of devices, furthermore, conventional intrinsic gettering procedures could not be adopted, as the entire volume of the silicon substrate is active with respect to the absorption of solar photons and to the associated photogeneration of carriers. As the cost of a solar silicon material should, at least in part, depend on its impurity content, considering that each impurity removing step costs in energy, investments and labour, one would be faced at first with the problem of defining the maximum amount of impurities tolerated for a given efficiency and then with the problem of removal the proper excess of impurity content.

The effective impact of the different impurities on the lifetime or diffusion length, and thus on the conversion efficiency of single crystal silicon solar cells, was one of the problems which were examined in full details at the Westinghouse Research and Development Centre [43, 44]. To this scope, standard samples containing single or multiple impurities were prepared from Cz-grown ingots suitably doped and then sliced to wafers, on which the chemical analyses and the electrical measurements were carried out. Details are reported in Ref. [45].

Figure 5 reports a summary of the results obtained by J. R. Davis et al. [44], which shows that the majority of the impurities of the eight group of the periodic Table are tolerated at sub-ppm levels, with the exception of Ti. Metallic impurities of the fourth and fifth group should be, instead present at sub-ppb levels.

One could therefore afford a definition of “solar grade” silicon on the assumption that the tolerated amount of impurity be below the threshold at which the normalized efficiency of a solar cell η/η^0 , where η^0 is the efficiency of a test solar cell fabricated with EG silicon, deviates from one.

It should be remarked that this definition holds only for single crystal silicon, as GB will behave as gettering sites for metallic impurities, which could be, therefore, partially or totally removed by the bulk

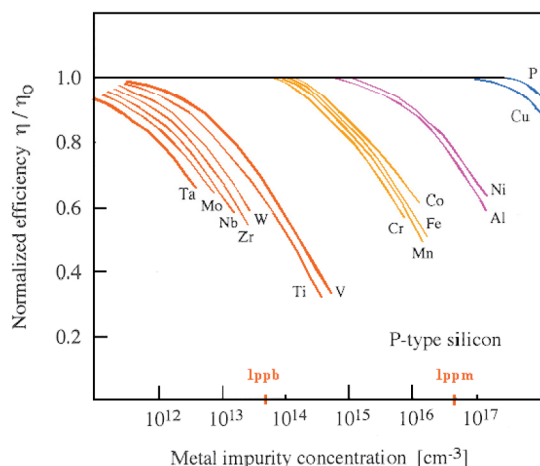


Fig. 5 (online colour at: www.pss-a.com) Effect of the metallic impurity content in single crystal silicon on the normalized efficiency of solar cells (after J. R. Davis, R. H. Hopkins, A. Rohatgi [44]).

of the grains by segregation processes. As before, here the problem is the effect of impurities on the electrical activity of GBs, which could be of limited or negligible relevance for GBs parallel to the drift and diffusion paths of majorities and minorities, but very detrimental for those lying orthogonally.

The influence of Ti, V, Cr, Fe and Zr on the PV behaviour of multicrystalline silicon was therefore studied by one of the present authors [46, 47] using an original approach in order to account simultaneously for the impurity contamination and the microstructure. It was assumed, in fact, that the product $L_{GB}N_D$, where L_{GB} (cm⁻¹) is the average length of the GBs on a square cm of the sample and N_D (cm⁻²) is the dislocation density, could be used to account for the influence of the GB-impurity interaction on the diffusion length.

The results of this investigation showed that at concentrations in excess of 10^{12} – 10^{13} cm⁻³ all these impurities, with the exception of iron, interact with extended defects, inducing a simultaneous decrease of the diffusion length.

Several attempts to monitor directly the segregation of metallic impurities at GBs has been carried out in the years, starting from the early works of Kasmerski et al. [48] and Kasmerski and Russel [49], who, using the scanning Auger microprobe and SIMS measurements, showed that (O, C), Ni, Al, Ti, Cu and Mg could be detected at fractured GBs at concentrations higher than 10^{18} cm⁻³, in comparison to bulk grain concentrations of the order of 10^{11} – 10^{15} cm⁻³.

Similar effects of Cu and Ni at GBs, possibly associated to the previous precipitation of oxygen, have been identified on $\Sigma = 25$ bicrystals annealed at 900 °C by Maurice and Coliex [50] using energy dispersive X-ray spectroscopy and EBIC measurements and by Ihlal et al. [51] on Cu- and Ni-contaminated $\Sigma = 25$, $\Sigma = 13$ and $\Sigma = 9$ bicrystals annealed at 1100 °C. These last authors were able to identify, using EBIC measurements, the formation of an about 100–150 μm thick denuded zone, on the both sides of the interface, and the formation of silicides precipitates in the bulk of the grains. Here, the authors tentatively correlate the gettering efficiency of individual GBs to the extension of the denuded zone by modelling the excess interface energy and of the associated strain fields.

The segregation of submicron-size precipitates of Cr, Fe and Ni in mc-Si in regions of high minority carrier recombinations, which could be reconnected to GB regions, was also detected by McHugo et al. using synchrotron based XR fluorescence [52]. The same authors clarified in a later paper [53], using the near edge structure of XR absorption spectra, that the iron precipitates consist of iron oxides or silicates, which are more stable than the corresponding silicide.

Similar experiments were carried out by Buonassisi et al. [54] for the analysis of copper-rich precipitates in silicon, who showed that copper is an ubiquitous contaminant of silicon and that its segregation features (composition of the phase) depend on the defective structure and on the oxygen content of the

silicon matrix. In addition, they showed also that in as grown mc-silicon copper-rich clusters were located at GBs, together with nickel and iron, all of which not intentionally added to the melt from which the ingots were solidified. As already anticipated by one of the present authors for the case of Er–O–dislocation interaction [55] it could be concluded that oxygen competes strongly with metals on the interaction with silicon atoms at the interface or at the boundary of an extended defect, depending on the Me–O, Si–Me and Si–O bonding energies. When Me–O bond formation prevails, extended defects work as heterogeneous nucleation centres [54].

These results might also be used to explain why extrinsic gettering processes using near surface phosphorous and aluminium deposition are shown to be not always useful in the case of mc-Si, while are very effective in the case of silicon microelectronic processes [56] as well as for impurity gettering from EG-dislocated silicon [57]. It can be argued that once the metallic impurities interact with extended defects giving origin to stable oxide or silicate bonds, their extraction by gettering processes is a very difficult task.

6 Towards the use of “solar grade” silicon

We have shown in the previous Sections that the requirements for the impurity content of a “solar grade” material are somewhat relaxed with respect to those of the EG silicon, but not compatible with a conventional MG silicon feedstock, with its thousands of ppm amount of deep metal impurities and ppm amounts of B and P.

To overcome at least partially the problem, we designed and operated a two step process, of which the first was the production of a high grade MG silicon via the carbothermic reduction of quartz with SiC (run HP6), or quartz and pellets of carbon black (run HP10), starting from very pure quartz and the second consisted in its subsequent refinement using one or two runs of directional solidification.

The carbothermic process was carried out in a 500 kVA furnace lined with high purity graphite, using high grade carbon electrodes, in order to suppress or at least reduce the unwanted impurity contaminations from the furnace materials.

Table 3 reports some typical results, which show that the MG silicon obtained by pelletized carbon black (MG HP10) presents better chemical properties than that prepared from SiC, but still too far from solar grade properties (see Fig. 5). In both cases a double DS purification was unable to reconduct the material to strictly solar grade properties.

It should be noted, however, that the source of most of the impurities found in the MG silicon was definitely found to be the atmosphere of the factory, where MG silicon and Si–Fe alloys were produced in conventional furnaces.

Solar cells fabricated on slices of the ingot of second solidification HP10 showed however an average efficiency of 6% against that of a lab cell fabricated with EG silicon showing a 10% efficiency. The best cell showed an efficiency of 6.6%, with an OCV of 549 mV, a short circuit current of 44 mA cm⁻² and a

Table 3 Impurity content (in ppm) of MG silicon in as-prepared conditions and after one or two purification steps.

element	MG-Si HP6 (*)	after one DS solidification	after two DS solidifications	MG-Si HP10 (**)	after one DS solidification	after two DS solidifications
Al	374	2.6	<1	107	5.1	2.08
B	13.9	12.4	10.4	15.3	6.7	8.0
P	14.7	1.8	3.3	10.6	4.8	5.9
Fe	615	<1	1.9	33	9	1.3
Mg	14	<1	78.5	32	14	16
Ca	49.7	39	>175	50	128	19
Ti	83	<1	<1	37	<1	<1

* From SiC and quartz.

** From black carbon and quartz.

FF of 68%. Making again reference to Fig. 5, with the level of impurities measured in the slice, we would instead expect normalized efficiencies close to 20% or less.

As forecasted, impurity segregation at GBs removes a large fraction of deep and shallow impurities from the grain volume, but the amount removed is not sufficient, however, to entirely suppress their detrimental role, also because of a non negligible role played by recombination at GBs.

7 Conclusions

We have shown that a “solar grade” silicon of MG origin might be adapted to photovoltaic uses, playing major attention to the furnace operation environment and to the compatibility of GB impurity gettering to high conversion efficiency.

We have also shown that the association of a casting process to a “solar silicon” feedstock is a promising but still challenging solution for the future, large scale application of photovoltaics. In favour of this solution are the almost unlimited availability of clean raw materials and the existing deep knowledge about the fabrication of MG silicon and about the properties of mc-silicon. The major drawbacks which still remain are the removal of donor and acceptor impurities, the careful control of unwanted contamination during the MG fabrication and the lack of one or more high speed silicon sheet growth processes specifically addressed at a solar grade feedstocks, which should associate the request of high throughputs to efficient impurity removal. We think that defect engineering procedures, already proven very effective in single crystal silicon, might be developed also for solar grade silicon on the base of the already deep existing knowledge, with major emphasis on the chemistry of the impurity/extended defect interaction processes in a multicrystalline material in the study of impurity removal or gettering, which was, until the most recent years, almost totally ignored or under evaluated. Of great help would be, under this respect, the development of a spectroscopical technique at the nanoscale level, for the detection of segregated impurities at GBs.

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