

Return of UMG-Si: a new hope

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ABSTRACT

Upgraded metallurgical-grade silicon (UMG-Si), once looked on as a cost-effective and energy-efficient alternative to Si produced via the Siemens route, has experienced a severe regression of late. This has been caused both by the market conditions and by specific physical properties of these materials. Meanwhile, the qualities and the rated influence of negative physical effects have changed partially. Hopes are again rising that these materials, which have to be compensated to meet the desired net doping specifications, might achieve an economical breakthrough instead of long-dreaded low breakdown voltages. In the following paper, we summarize a few of our results on multicrystalline UMG silicon as well as results published by other research groups in the last few years.

Introduction

In May 2011, for the first time in history, a member of the German Green Party was elected to the head of government of a German federal state. Together with the national Renewable Energy Law which defines guaranteed feed-in tariffs, and the gradual political change in thinking, this could mean that the energy turnaround from fossil to renewable energy sources will speed up significantly. Photovoltaics is also included as an important element, especially in combination with wind energy, even in spite of the solar irradiation which is low in comparison to southern European countries [1].

If the feed-in tariffs for solar power are transformed as intended, grid parity will be achieved by 2012 in agreement with last year's forecast by Breyer [2]. The planned increase of renewable energies means increased development of the European electricity networks as well as energy accumulators, and significant cost reductions for photovoltaic systems. Meanwhile, there are about 100 relevant enterprises that deal with the production of silicon for solar cells. One option for new silicon factories for solar cell requirements is compensated UMG-Si, although Bernreuter forecasts less than 1% of market share for UMG-Si in 2012 [3]. Depending on material and manufacturing processes, the terms solar-grade silicon (SoG-Si) and UMG-Si are also used in this context with varying meanings.

'Solar-grade silicon'

Just a few years ago, UMG-Si was discussed as a promising approach to the solar industry to cover the immensely growing demand for solar silicon. As a result of setting up many new solar silicon factories, the high price for highly purified silicon collapsed in 2009 and thus brought UMG-Si production to the edge of profitability. In the same year, Calisolar and PV Crystalox Solar started their new line productions, while other solar cell producers like Canadian Solar and Q-Cells SE reduced their UMG solar cell production. Silicon

manufacturers like Timminco or Dow Corning nearly stopped their production of UMG-Si altogether. In addition, UMG-Si was becoming more and more associated with the danger of hot spots due to low breakdown voltages. This trend remained unchanged despite the proposed treatment of symptoms with, for example, bypass diodes [4]. This could be one reason why most companies switched to different titles for their materials instead of the term 'UMG-Si'. More importantly, the quality of their materials has now changed greatly. In general, UMG-Si means that metallurgical silicon is cleaned by metallurgical methods instead of the chemical cleaning via the Siemens process.

“SoG-Si means that the material's purity is sufficient for use in solar cells, regardless of metallurgical or chemical cleaning.”

SoG-Si, on the other hand, means that the material's purity is sufficient for use in solar cells, regardless of metallurgical or chemical cleaning [5]. Ten years ago, UMG-Si typically featured a purity of about 99.99% which is nearly achievable for a pure metallurgical feedstock [6]. UMG-Si wafers were tested as substrates for thin-film LPE solar cells [7]. For use as solar silicon, UMG-Si with such a low purity is only a preliminary stage to SoG-Si. Photosil used the term UMG-Si in this way in an article in the ninth issue of *Photovoltaics International* [8]. However, these processes were often improved to such an extent that some sorts of UMG-Si could be used directly as SoG-Si without further treatment. Therefore the term 'solar-grade silicon' better reflects the changed material properties. For example, the SoG-Si from 6N Silicon – which is currently merging with Calisolar – claims to reach a purity of up to 99.9999% via a sequence of aluminium glazes with a subsequent acid bath [9, 10]. Therefore, the material quality might be well suited

to solar cells – at least if the content of aluminium is mastered. The first promising results of solar cells with efficiencies of well above 16% have been presented [10], illustrating that it is difficult to compare the results from UMG-Si materials today and in the past. To do so, the concentrations of impurities and dopants would have to be considered, which are not always revealed by manufacturers. This has to be kept in mind considering the following results.

The use of pure metallurgical feedstock is essential. The above mentioned cleaning refers not only to the concentration of metals, but also to the dopant concentration. In contrast to the silicon which was produced via the Siemens process, UMG-Si feedstock contains generally high fractions of both boron and phosphorus. The total impurity contents remain unchanged without chemical cleaning during crystallization. Metals tend to stay mainly in the melt during crystallization and move with the crystallization front to be enriched in the upper part of the ingot.

On the contrary, the dopants boron and phosphorus are strongly incorporated into the crystal due to their higher segregation coefficients. Their concentrations increase with the height in the ingot for slow crystallization according to the Scheil equation. Since phosphorus segregates stronger than boron, it accumulates in the remaining melt while boron is more easily incorporated in the crystal yielding a p-type net doping of the crystal. At a certain height of the crystallized ingot, the phosphorus concentration exceeds the boron concentration in the melt to such an extent that the same amount of phosphorus and boron is incorporated in the crystal. With a net doping concentration of zero, the bulk resistivity is at its maximum here. Above this point, the local surplus of phosphorus leads to an inversion of the polarity type yielding n-doped material with a high impurity concentration, due to the upwards segregated metals. This explains why the n-type part is typically cut off and not used for the production of solar cells. The wafer

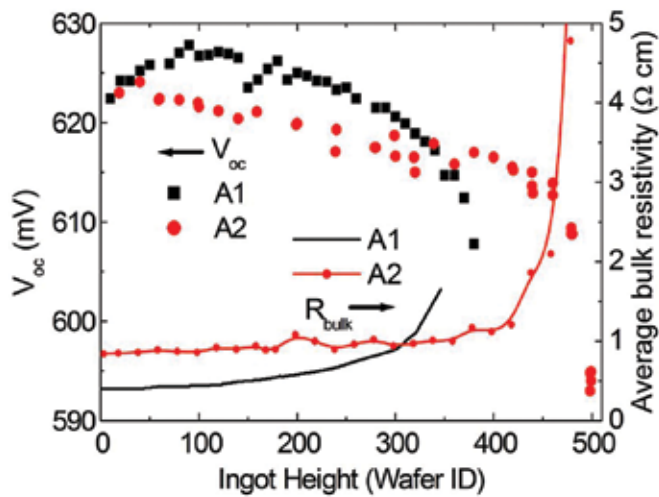


Figure 1. Comparison of open circuit voltage and average bulk resistivity for materials A1 and A2 [13].

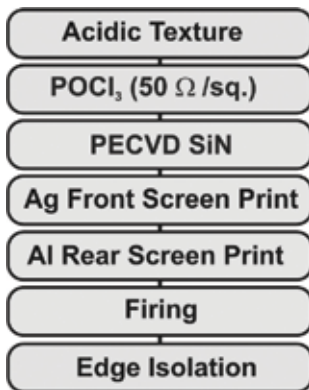


Figure 2. Process flow for the presented multicrystalline UMG-Si solar cells.

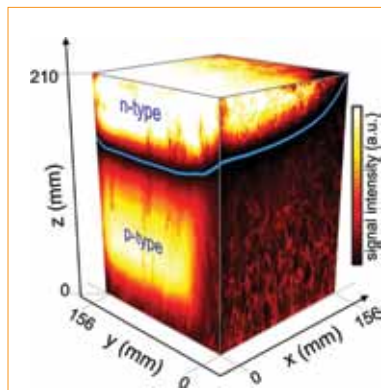


Figure 3. Composition of PL images from the side faces of a UMG mc-Si brick including a type inversion [11].

Courtesy of J. Haunschild, Fraunhofer ISE

Net doping

The resistivity which is induced by net doping B-P has a strong influence on open circuit voltage (as can be seen in Fig. 1) of materials A1 and A2. Both materials are p-type wafers from the edges of two different multicrystalline 100% UMG-Si ingots from the same supplier. All wafers shown were processed to screen-printed $12.5 \times 12.5\text{cm}^2$ solar cells according to a typical industrial solar cell process (Fig. 2).

Higher ingot positions mean a lower net doping and therefore higher resistivities. This in turn leads to a smaller splitting of the quasi-fermi levels which means a decrease of the open circuit voltage V_{oc} . This is also the reason why V_{oc} starts at a lower level for material A2 compared to material A1, although other factors may also decrease the V_{oc} . These materials cannot be compared to the Photosil materials because the impurity concentrations are unknown to us.

Besides the variation in height, the resistivity also changes for wafers from the same ingot height. This is a consequence of the crystallization process. Horizontally inhomogeneous cooling down leads to a non-planar crystallization front, the efficiency of which depends on the heating mechanism and the possibilities for varying the local temperatures of the crucible furnace. The crystallization of silicon that is in contact with the crucible can be controlled easily, but it is difficult to induce a homogeneous horizontal crystallization. As a result, this varies resistivities for wafers from the same height but different horizontal positions may occur.

An example of such an inhomogeneous crystallization can be seen in Fig. 3. These photoluminescence images of the surfaces of a brick from a small ingot were measured and assembled for a 3D impression by Haunschild at Fraunhofer ISE and illustrate the variations of resistivity and lifetime for a small ingot. The blue line indicates the location of the type inversion. Wafers from the upper part of this ingot will consist of both p- and n-type parts, a material which is ineligible for cell production [11]. This spatial inhomogeneity could be reduced substantially by a better control of the crystallization in the meantime. For larger ingots, a lower spatial resistivity variation is possible, as can be seen in a comparison of material from a centre and an edge brick of the same ingot [12]. For further investigation, it is necessary to measure the resistivities of the wafers with a spatial resolution instead of the average values shown in Fig. 1. The selection of the measured wafers and solar cells from different heights is illustrated in Fig. 4. The resulting measurements, e.g. the resistivity maps, are shown in Fig. 5 [13].

yield of an ingot is mainly defined by the concentrations of boron and phosphorus. In order to reach acceptable resistivities,

boron must usually be added and the resulting material is called compensated silicon.

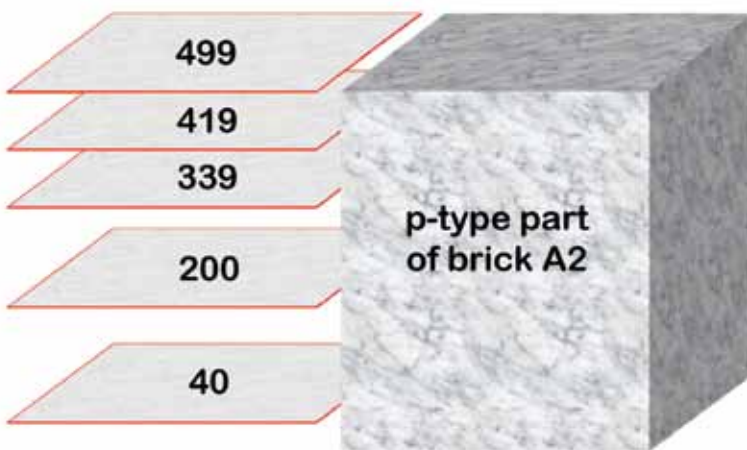


Figure 4. Scheme of the wafer positions of the processed wafers which are shown in Fig. 5 [13].

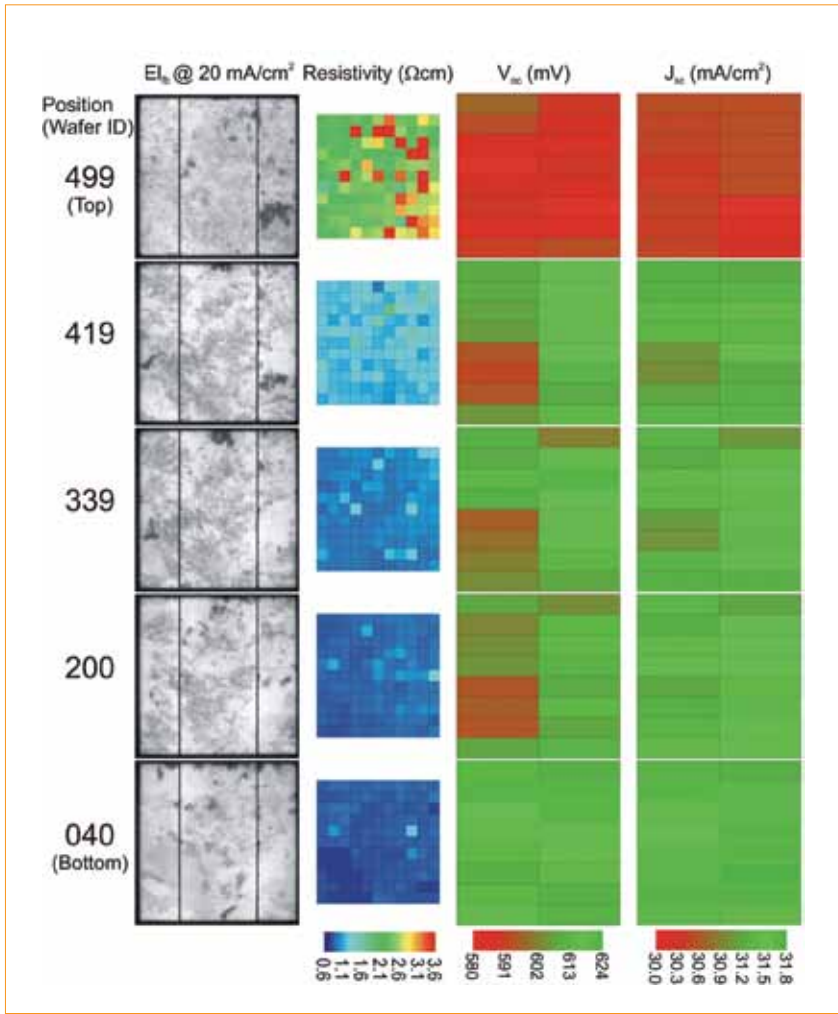


Figure 5. Survey of the measurements on sawn sample solar cells from material A2 in relation to the ingot height position [13].

The edges of the wafers are not included to avoid systematic errors for the resistivity. The lower sides of the images correspond to the former ingot edge where the measured resistivity is only slightly lower. Large spatial variations are only observed for wafer 499 from the highest position of the p-type part. Here, the measured bulk resistivities also differ from the measured value in Fig. 1, and to a much greater extent than for the other wafers, where the resistivity is about 0.6 to 1.6Ωcm. The comparison with the resistivity map of a vertical cut (shown in Fig. 6) from the edge of the same brick verifies these measurements and also indicates possible homogeneity problems during the crystallization at the edge.

Although it is unknown to us how much of the ingot's top part was cut off, the deviation for the highest part is probably due to the increased impurity concentrations, as measurements using the Seebeck effect proved that this material is still below the type inversion. High impurity concentrations mean that the inversion point is placed higher than for A1. This is then combined with a higher wafer yield, not or not only caused by an increased ingot height. This is in

agreement with the behaviour of the short circuit current density J_{sc} in Fig. 7 which is in contrast to the following results.

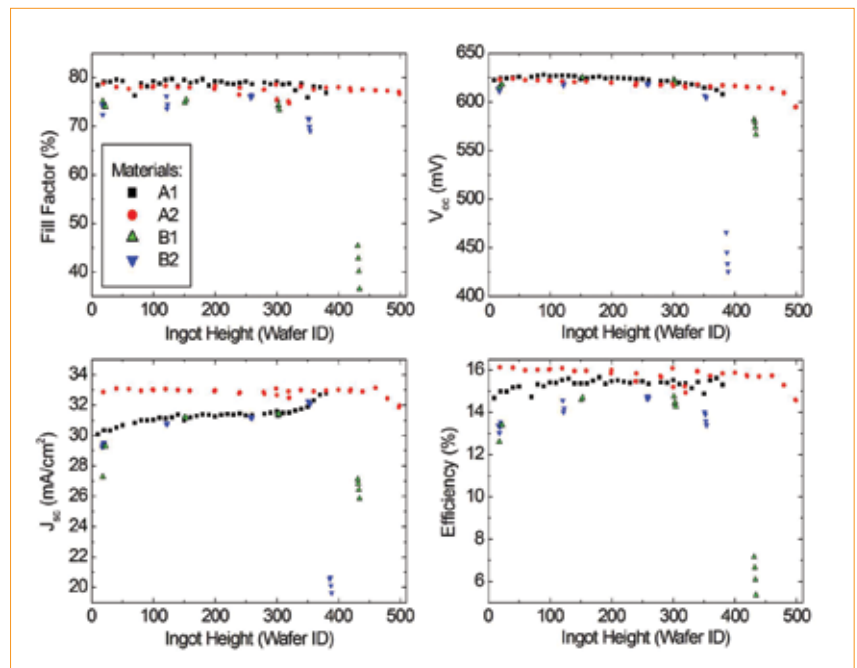


Figure 7. IV parameters for the solar cells processed with materials from two ingot suppliers A, B relative to the vertical position in the ingot [13].

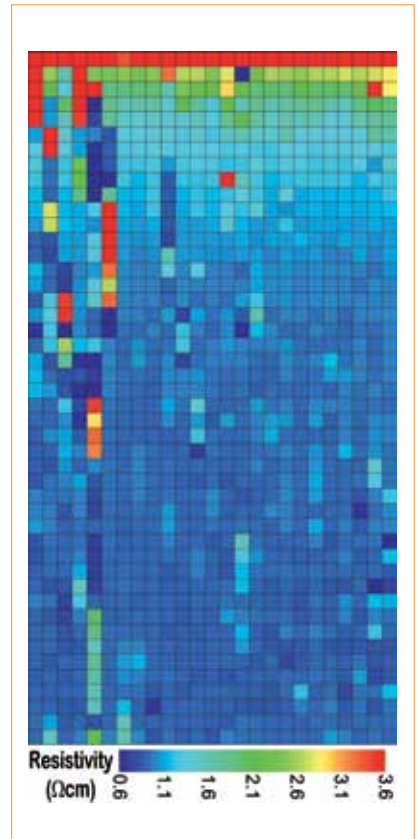


Figure 6. Resistivity map of a vertical cut from brick A2.

While the J_{sc} of A2 is stable also in the upper part, for the first UMG-Si material from the same supplier, A1, we found an increase of J_{sc} towards the inversion level. The materials B1 and B2 were cast as small test ingots as shown in Fig. 8 for the German SolarFocus project [14] and showed the same behaviour for the bulk resistivities. This is in agreement with the



Figure 8. Example of a small ingot casted by SolarWorld AG for the SolarFocus project in 2008, similar to the ingots of the materials B1 and B2 in Fig. 7.

Courtesy of SolarWorld AG.

are rather stable, the electroluminescence (EL) images under a forward bias of $20\text{mA}/\text{cm}^2$ (Fig. 5) show more dislocations and the spatially inhomogenous formation of recombination active clusters of crystal defects are shifted towards the centre of the original ingot with increasing height. EL reverse bias images at -10V as well as dark lock-in thermography (dLIT) measurements revealed that these clusters were also areas of increased shunting [13].

To understand these contradicting properties of the A2 solar cells, several of them were cut into smaller cells. For the resulting J_{sc} and V_{oc} maps (Fig. 5), the total J_{sc} is about $2\text{mA}/\text{cm}^2$ lower than for the entire cells mainly due to the lack of a suitable IV calibration for these small cells (because of size and reflection) resulting in a too-low illumination intensity. Both the V_{oc} and especially the J_{sc} map indicate worse values for the small solar cells, which showed a growing defect cluster as well as an increased dislocation density in the left part of the images. In contrast, the cluster on the right side does not influence the IV parameters significantly. This might be explained by the simultaneously improving influence of the dislocation free area right next to this cluster. At least for these solar cells, the results might be even better for a lower dislocation density, which is a matter of improved ingot casting. As a result, the remaining variation of efficiencies for

this material is caused by the decrease of the open circuit voltage, mainly due to the increased bulk resistivity [13]. This is probably the main obstacle for height-independent efficiencies and also for a further increase of the wafer yield. Both might be solved by the systematic addition of boron to the melt during crystallization, although this is difficult to control. However, there are further properties that differ for compensated silicon compared to electronic-grade silicon.

Bulk lifetime and mobility

Reductions in the bulk lifetimes and mobilities are reported in compensated silicon in comparison to electronic-grade silicon with the same net doping concentration, due to compensation and the related increased scattering of charge carriers by the dopants. The increasing resistivities towards the type inversion can cause higher bulk lifetimes because the lifetimes are connected to the net doping concentration [18–20]. High contents of metal should also reduce the minority carrier lifetime significantly.

Hot spots and breakdown voltages under reverse bias

According to the results of Kwapil et al. and Breitenstein et al., at least three different

well-known increase of internal quantum efficiencies for long wavelengths (as shown in Fig. 9) [12, 13].

For compensated material, J_{sc} seems to depend on the net doping concentration. One possible explanation is the formation of B-P pairs, which have been suggested by several authors [15–18]. As mentioned, we assume for A2 that the inversion level was shifted further to the top part of the ingot. This probably increased the wafer yield so far that the solar cells from this part are close to the top of the ingot and already have a relevant impurity concentration. While J_{sc} and V_{oc} in Fig. 7

*True Solar Grade Silicon
with low carbon footprint*



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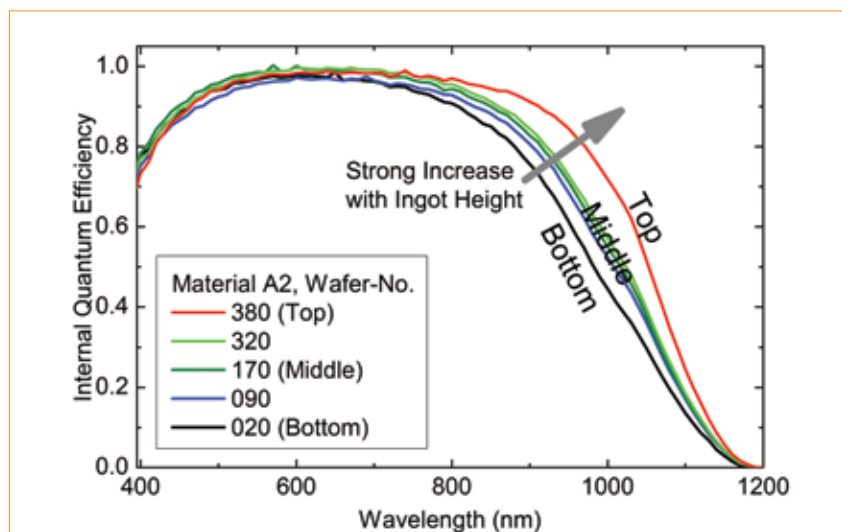


Figure 9. Internal quantum efficiency (IQE) for the material A1 versus the wavelength clearly shows the relation to the J_{sc} due to the increasing bulk resistivity [12].

breakdown types under reverse bias can be distinguished in multicrystalline silicon solar cells, not only for UMG-Si.

The 'early' breakdown type occurs in the range between -5 to -7V at 'singular spots' which seem to be process-induced and do not lead to high leakage currents. The 'soft' breakdown right above this voltage level is related to the crystal defect structure and appears mainly at recombination-active dislocations or grain-boundaries. As these recombination-active regions are caused by impurity decorations in general, this breakdown type dominates in areas of higher metal contaminations in the material [21]. Breitenstein distinguishes for these soft breakdown sites between weakly and strongly contaminated crystal defects. For UMG-Si it can be concluded that whether or not soft breakdown is of importance depends greatly on the impurity content. For typical impurity concentrations and realistic voltages under reverse bias, the reverse current is low. A further observation is that the reverse breakdown voltage, at which the soft breakdown occurs, is lower for rougher (e.g. acidic-etched) surfaces compared to rather flat surfaces. This is relevant for multicrystalline solar cells in general [22].

At a reverse bias exceeding -13V, an avalanche-dominated breakdown is also observed for acidic textured materials at etch pits located around dislocations. Due to strongly increasing currents under reverse bias, this 'hard' breakdown type turns out to be the most dangerous, but can probably be reduced by improved texturization. For UMG-Si solar cells, the influence of the bulk resistivity seems to predominate for reverse biases [23]. Metal contents and crystal defects in contrast only seem to be detrimental at high impurity concentrations [24]. Thus it may

be concluded that the breakdown under reverse bias is again strongly affected by the feedstock and cleaning process.

Degradation effects

Light-induced degradation (LID) refers to the decrease of the efficiency under illumination. The best known form of LID is due to the formation of boron-oxygen complexes which act as efficient recombination centres and therefore reduce the lifetime in the bulk. According to Bothe's empirical equation, the upper limit of the lifetime decreases approximately with the increase of [B] and $[O_i]^2$ [25]. The formation of these recombination centres require both of the elements, so that the LID at a fixed concentration of boron can be assumed to follow the oxygen concentration quadratically. Although standard multicrystalline silicon contains less oxygen than Czochralski-grown silicon (Cz-Si), the concentrations of both elements can be higher in UMG-Si. This makes LID an issue that has to be considered at least in qualitatively high material. Due to its high segregation coefficient, oxygen is preferentially incorporated in the crystal and is therefore primarily present in high concentrations in the lower part of the ingot while the boron and phosphorus concentrations increase towards the top. In fact degradation can be serious if the oxygen concentration exceeds a certain value. The degradation can only be improved by an adjusted crystallization.

Degradation is reported to be in the range of 1%_{rel} or even lower [10, 26, 27]. This can be explained first by further cleaning steps for the feedstock material that reduce the content of impurities, and second by the formation of boron-phosphorus pairs (mentioned above).

According to this proposed model, many of the boron atoms pair with phosphorus atoms which means that they are not available for the formation of B-O recombination centres during illumination [15, 17, 18]. For compensated Cz-Si, another defect model can explain the dependence on the net doping concentration instead of the electrically active boron concentration by focussing on the concentration of interstitial instead of substitutional boron in B_iO_{2i} . Metals (except alkali metals) do not present an obstacle for the use of UMG-Si due to their effective segregation to the very top part of the ingot. For lower metal and oxygen concentrations, the LID does not differ widely from the results for multicrystalline solar cells made from electronic grade silicon. Any potentially remaining degradation could vary for different ingots and even for solar cells made from different ingot heights. One way to deal with this is an 'electrically-induced pre-degradation' that proceeds much faster than light-induced degradation [29].

Efficiencies

Finally, as the wafer yield, LID and the low breakdown voltages seem to be manageable, solar cell efficiency affects profitability strongly. Good results have been obtained by several groups in recent years, but the best reported efficiencies for industrial-sized solar cells were still limited to a range of 16.1 to 16.4% – still below the typical reference efficiencies [10, 12, 27, 29, 30]. Efficiencies up to 18.5% could be reached only with specialized high efficiency cell processes on lab-type $2 \times 2\text{cm}^2$ solar cells [31, 32]. Now, in April 2011, Engelhart has reported for Q-Cells the successful production of large-scale solar cells in the same efficiency range, with the best efficiency being 18.35% for a 6" UMG solar cell and a median of about 18% for wafers from the whole p-type part [33]. So it seems that UMG-Si is back on the road to success. Time will tell if it will also be an economical success for the different UMG-Si solar cell producers and feedstock suppliers.

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