n-type multicrystalline silicon for high-efficiency solar cells

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ABSTRACT

High-efficiency silicon solar cells require silicon wafers of high electrical quality as the base material. One advantage of n-type compared with p-type doped silicon is the smaller impact of many metal impurities on the electrical material quality. This applies especially to n-type multicrystalline silicon ingots produced by the directional solidification process, with dissolved metal impurities typically introduced by the crucible system. Investigations of the efficiency losses in n-type multicrystalline silicon solar cells showed that recombination-active crystal defects, such as dislocations, are the dominant limitation of quality in terms of electrical properties. By developing a solidification process with silicon granules as the seed material, high-performance multicrystalline silicon with a low number of dislocation networks, and thus a high electrical material quality, was produced. The applicability of a high-efficiency n-type solar cell concept with a full-area tunnel oxide passivated rear contact (TOPCon) on this type of material was investigated. A TOPCon solar cell with a record efficiency of 19.6% on n-type high-performance multicrystalline silicon demonstrated the potential of this class of material. By improving the front-surface texture and adapting the emitter formation process, it is expected that efficiencies of the order of 22% will be possible on n-type multicrystalline silicon in the near future.

Introduction

The increase in solar cell efficiency has been identified as an important aspect for further cost reduction in photovoltaics. To date, the highest efficiencies of solar cells on silicon wafers have been achieved on n-type monocrystalline silicon (mono-Si) substrates, with record efficiencies exceeding 25.0% [1]. This is partly because of the absence of a cell degradation effect which reduces the efficiency in p-type mono-Si and is caused by the metastable boron–oxygen complex. This effect can be avoided by the use of n-type silicon with phosphorus as the dopant material.

The push for higher cell efficiencies is not limited, however, to just mono-Si; solar cells on multicrystalline silicon (mc-Si) will also need to demonstrate high efficiencies in the future. The latest results obtained for large-area p-type mc-Si solar cells show that efficiencies above 21.0% are achievable with cell processes suitable for mass production [1]. This is of great importance for the PV market, since solar cells on multicrystalline silicon wafers actually dominate the market, with a share of about 65%, because of cost-competitive production technologies.

> "The development of n-type mc-Si as a possible material for cost-effective high-efficiency cells has gained new momentum."

The combination of cost-efficient mc-Si wafers with the advantages of n-type doped substrates has been previously investigated in various material studies. The electrical quality of n-type mc-Si, as in the case of n-type mono-Si, is less inhibited by typical impurities, such as transition metals, than p-type material [2]. Because of the specific capture cross sections of electrons and holes for important metal-related defects, such as interstitial iron Fe_i, their detrimental effect on minority-carrier lifetime is greatly reduced in n-type material; this leads to a higher efficiency potential, under the assumption of comparable cell concepts [2]. However, the lack of appropriate cell concepts and production processes for n-type mc-Si has been hindering this research path in the past. With the development of high-efficiency cell processes for n-type substrates employing low-temperature processes or full-area passivated back contacts, such as heterojunction [3] or TOPCon cells [4], the development of n-type mc-Si

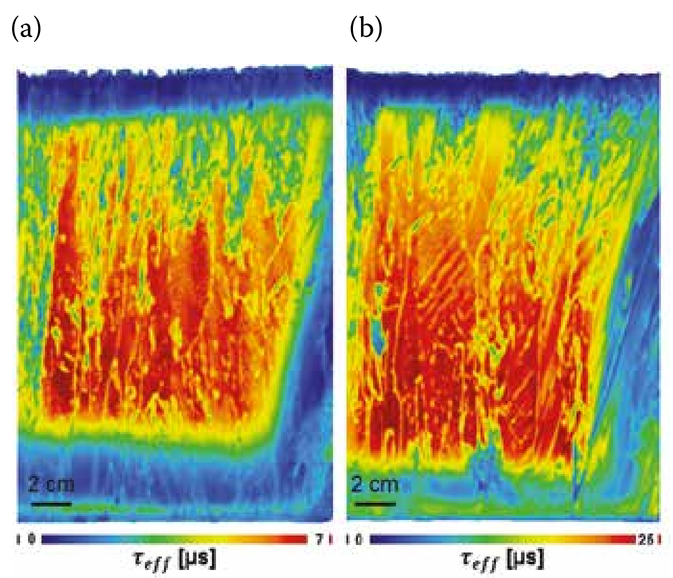

Figure 1. Spatially resolved effective minority-carrier lifetime at the side face of (a) one p-type and (b) one n-type mc-Si edge brick, measured by the MW-PCD technique.

as a possible material for cost-effective high-efficiency cells has gained new momentum.

After a short review of the material-related losses of p- and n-type mc-Si with respect to suitable solar cell concepts, the focus will be on the development of improved ingot-casting processes for n-type mc-Si. The first solar cell results with high-efficiency cell structures on these materials are presented.

Efficiency losses in standard p-type and n-type mc-Si

The production of n-type mc-Si wafers relies on the same basic processes as the ones for p-type material. Ingots can be grown using the same directional solidification techniques as standard material today, but with the use of phosphorus instead of boron as the dopant species. The preparation of bricks out of these ingots, and the subsequent processing steps until the final wafer is created, are identical to the p-type methods. However, a comparison of the material characteristics of p-type and n-type multicrystalline material reveals significant differences.

Fig. 1 shows the distribution of the effective minority-carrier lifetime τ_{eff} measured on the side faces of (a) one p-type and (b) one n-type standard mc-Si edge brick of G2-size ingots grown using the same directional solidification process. The lifetime was measured by a Semilab WT2000D tester using the microwave photoconductance decay (MW-PCD) method at the polished, but otherwise unpassivated, brick sides, with the ingot edge visible on each of the right sides. Despite the strong limitation of the measured effective lifetime by recombination at the brick surfaces, differences in the bulk minority-carrier lifetime between p- and n-type mc-Si are clearly noticeable. The measured lifetime values for the centre part of the n-type ingot are up to a factor of four higher than comparable regions in the p-type ingot (note the different scales for p-type and n-type brick sides); this represents the previously discussed difference in minority-carrier recombination due to introduced impurities. The zone of reduced lifetime at the bottom of the ingot as a result of the in-diffusion of impurities after solidification is smaller for n-type material, albeit the zones near the ingot edge have a comparable width. A closer inspection of these materials reveals that dislocations in the edge region are a significantly limiting factor in the case of the n-type ingot [5].

The resistivity profiles over the ingot height, measured at the ingot centre, show that the resistivity spread for the n-type ingot is greater by a factor of four (Fig. 2). The reason for this is the smaller segregation coefficient of phosphorus (k_0 = 0.35) than that of boron (k_0 = 0.8), which leads to a stronger piling-up of dopants in the liquid phase as the solidification advances from bottom to top.

Whereas lifetime in the as-grown state can yield valuable information (e.g. about the crystallization process), the minority-carrier diffusion length L_D after high-temperature processing [6] is more important for evaluating material quality with respect to final solar cell efficiency. As minority-carrier mobility in p-type silicon is greater than in n-type silicon by a factor of approximately two to three, the minority-carrier lifetime in n-type silicon has to exceed minority-carrier lifetime in p-type silicon by the same factor in order to achieve similar minority-carrier diffusion lengths in both materials. An analysis of the diffusion length images of standard n-type mc-Si wafers after the boron diffusion used for emitter formation on n-type solar cells reveals that very high local diffusion length values of up to 1,400µm can be achieved inside larger grains (Fig. 3). In contrast, large regions of small grains and dislocation

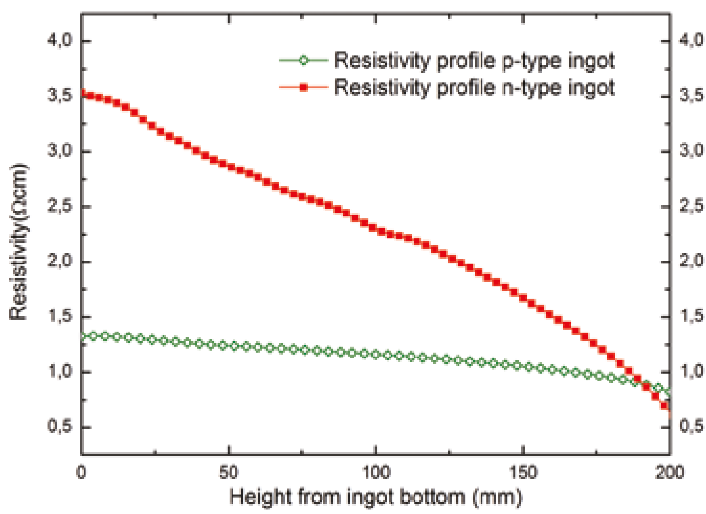

Figure 2. Resistivity profiles of one p-type and one n-type mc-Si brick, measured by the EddyCurrent technique, illustrating the different ranges in resistivity.

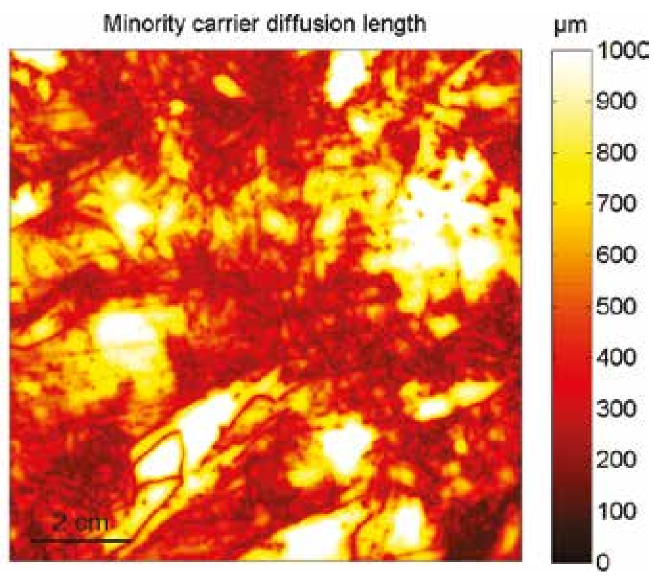

Figure 3. Minority-carrier diffusion length image of a standard n-type mc-Si wafer (10cm × 10cm) after boron diffusion at an irradiation of 0.05 suns, taken by calibrated PL imaging.

networks, visible as dark tangles, show strongly reduced diffusion length values and thus reduced local efficiency in the final solar cell.

A thorough investigation of the efficiency potential of p-type as well as n-type mc-Si materials [2,7] separated the expected material-related losses in high-efficiency cell structures due to homogeneously distributed defects (such as dissolved transition metals) from those due to decorated structural defects (such as dislocation networks and grain boundaries) (Fig. 4). Wafers made from the above-mentioned G2-size p-type and n-type standard mc-Si ingots received typical high-temperature process steps appropriate to the particular cell structure. This treatment ensures that expected changes in material quality during processing due to the gettering effects of impurities during emitter formation and due to impurity dissolution during contact firing are carefully taken into account. The p-type wafers received a phosphorus diffusion by $POCl_3$, as used for emitter formation, with a subsequent firing step; the n-type wafers were treated with a BBr_3 diffusion step without subsequent firing. Further details of the processing and material analysis can be found in Schindler et al. [2,7].

The analysis shows that, in p-type mc-Si material, most of the expected losses in cell efficiency are due to distributed recombination centres, far outweighing the losses due to recombination at decorated structural crystal defects. In the case of the n-type mc-Si wafers analysed, the situation is the opposite, with the recombination at crystal defects being the more pronounced class of defect.

From this investigation it has been concluded that a significant reduction in structural defects should allow the use of n-type mc-Si material for high-efficiency solar cells. Note that the application of a phosphorus diffusion can further reduce the losses in n-type mc-Si [2,7]. A detailed analysis of the limiting material defects, and of the impact of structural defects on carrier lifetime, in n-type multicrystalline silicon can be found in Schön et al. [5].

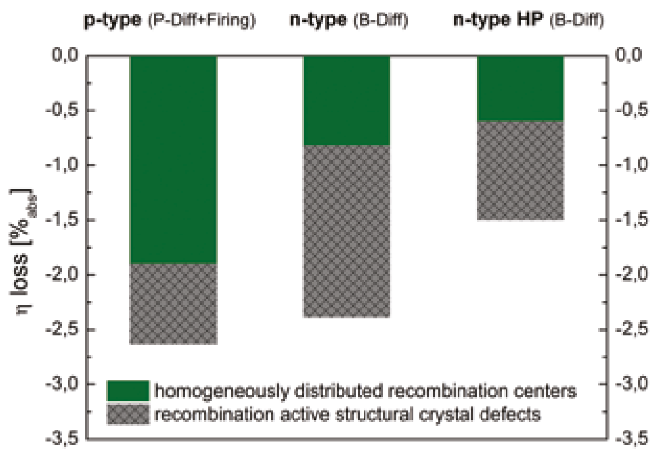

Figure 4. Material-related losses in p- and n-type standard mc-Si wafers from the ingot centre (without edge-region influence) for a high-efficiency cell structure with a cell efficiency limit of 21.8% [2] after typical processing steps. For comparison, the significantly reduced material-related efficiency losses in n-type high-performance (HP) mc-Si for the same cell structure are included in the graph.

Figure 5. Photograph of the cross section of a crystallized G1 ingot with a typical HP mc-Si structure. The unmolten feedstock can be seen at the bottom of the ingot.

> "To reduce the number of structural defects, a crystallization process for high-quality n-type mc-Si was developed using granular silicon as seed material."

Directional solidification of n-type high-performance multicrystalline silicon

In order to reduce the number of structural defects, and especially dislocation networks, a crystallization process for high-quality n-type mc-Si was developed using granular silicon as seed material. For the directional solidification processes, a Multicrystallizer VGF 632 Si furnace by the company PVA Tepla was used. The furnace, initially built for G4-size ingots (equivalent to 250kg of silicon), was retrofitted with a new hot-zone design for the solidification of research ingots of sizes G1 (equivalent to 15kg) and G2 (equivalent to 75kg).

Commercially available high-performance fused silica crucibles of G1 size, with a pre-coated silicon nitride lining, and high-purity polysilicon feedstock were used in all the experiments in this development. In comparison, the standard material discussed in the previous section was solidified in similar fused silica crucibles with a standard quality only. As seed material, silicon granules from a fluidized bed reactor process were placed at the bottom of the crucible prior to filling with polysilicon feedstock. Heavily phosphorus-doped monocrystalline silicon chunks from semiconductor applications served as the dopant material.

During the melting phase, the thermal process is steered in such a way that the feedstock material becomes molten from top to bottom. A small amount of granular material is left unmolten to act as seed material, forming an initial crystal structure with uniformly distributed small grains directly above the seed interface. The grains enlarge with increasing height, as seen in the cross section of a G1 ingot produced by this process (Fig. 5). Multicrystalline silicon material from this type of process has been introduced into the market as high-performance multicrystalline silicon (HP mc-Si) [8].

Because of a mean initial grain size of the order of $1\,mm^2$, or even less than that, the mechanical stress due to thermal instabilities near the solid–liquid interface can be minimized; the initiation, multiplication and spreading of dislocations is thus diminished. Fig. 6 shows photoluminescence (PL) images of wafers from the upper regions of n-type mc-Si ingots: the image in Fig. 6(a) is of a standard mc-Si edge brick of a G2-size ingot; the one in Fig. 6(b) is of a HP mc-Si centre brick from a G1-size ingot. The grain boundaries are visible as thin black lines against a grey background; dislocation networks or areas with a high density of subgrain boundaries are visible as regions of darker contrast.

In the standard mc-Si wafer (Fig. 6(a)), a large number of dislocations can be found near the ingot edge (left border of the image) as well as in various regions throughout the wafer. A combination of large grains and small grains is typical for this material: the microstructure of the material is therefore very inhomogeneous.

In contrast, the HP material (Fig. 6(b)) has very few regions containing large numbers of subgrain boundaries or dislocation networks. The medium grain size, calculated by image analysis, is enlarged to about $8\,mm^2$ at this ingot height; thus, the number of structural defects in this material is significantly reduced. The intensity of the background signal inside the grains depends on the intragrain carrier lifetime and on the local dopant density. In order to adjust the target doping concentration, and thus the bulk resistivity, the incorporation of impurities from the crucible system and the furnace atmosphere have to be taken into account.

For n-type material the incorporation of boron, either from the crucible material or via volatile species, could lead to a slight compensation of the free-carrier concentration introduced by the intentional phosphorus doping, thus changing the material resistivity. Variations in the net doping are visible in Fig. 6(b) as larger structures with a slightly higher intensity. This type of structure can be observed in various n-type mc-Si materials, irrespective of the seeding procedure. A spatial analysis of wafers from different ingot heights indicates a connection between this type of structure and the form of the solid–liquid interface. However, the effect of these slight variations on material quality, and thus on solar cell efficiency, seems to be weak.

An evaluation of the efficiency potential of lifetime samples fabricated from this material, analogous to the evaluation of the standard n-type mc-Si samples in the previous section, shows that losses due to recombination-active structural crystal defects could be reduced significantly (see Fig. 4). Thus, reducing the formation of recombination-active structural crystal defects by applying an advanced crystallization process leads to a considerably higher efficiency potential. The use of a higher-purity crucible in this experiment is also reflected in the reduced losses due to homogeneously distributed recombination centres (see Fig. 4). For future development, further optimizations of grain structure and reductions of impurity incorporation should lead to even higher material quality.

Manufacture of high-efficiency TOPCon solar cells

The introduction of the passivated emitter rear cell (PERC) structure to the solar cell market has opened up new efficiency levels for multicrystalline silicon materials. Trina Solar published cell results for their PERC solar cell on p-type HP mc-Si material with a record efficiency of 21.25% [1]. A characteristic feature of this cell architecture is a network of local point contacts at the back side of the solar cell. This poses a possible drawback for multicrystalline material, since the lateral current flow inside the bulk wafer may be hindered by grain boundaries which are typically decorated with impurity atoms and can react as barriers.

In contrast, the structures for high-efficiency cells with a full-area back contact architecture – such as heterojunction cell technology [3] or the recently developed tunnel oxide passivated rear contact (TOPCon) cell [4] – imply a one-dimensional current flow inside the bulk, perpendicular to the wafer surfaces. Since almost all the grain boundaries in HP mc-Si wafers are virtually perpendicular to the wafer surfaces (they have only small angles of tilt), the negative effect of structural bulk defects on the performance of a TOPCon cell should be smaller than in the case of PERC cells. Additionally, the TOPCon cell concept is a suitable candidate for the fabrication of high-efficiency silicon solar cells, as recently shown by Fraunhofer ISE's achieving a record efficiency of 25.1% [1,9].

To investigate the potential of n-type HP mc-Si as a substrate for high-efficiency solar cells, a series of 2cm × 2cm TOPCon cells were processed at Fraunhofer ISE. Wafers with a thickness of 180μm were cut from a G1-size ingot that had been crystallized by the developed HP mc-Si process. After standard wet-chemical texturing, the wafers received a diffused boron emitter on the front side and the TOPCon layer stack on the rear. The metallization scheme included a standard H-shape grid on the front side and a full metallization on the rear. In comparison with the process flow established for monocrystalline silicon, the wet-chemical texturing and the emitter diffusion process via a BBr_3 diffusion were different because of the material characteristics of mc-Si. Finally, the cells received a double-layer anti-reflection coating (DARC) on the front side. (Details can also be found in Schindler et al. [7].)

The cell parameters of the best solar cell are listed in Table 1. An efficiency of 19.6% could be reached, which significantly exceeds previously published values [7,10]. The measured V_{oc} of 663.7mV is suitable for high-efficiency solar cells. The measured J_{sc} of 38.87mA/cm² is of a high level with regard to the standard isotextured front surface. However, because of processing issues during plating, also observed on the float-zone (FZ) reference cells, a low fill factor of only 75.9% limited the overall efficiency.

The map of the short-circuit current density, depicted in Fig. 7, identifies the residual grain boundaries as the principal remaining limitations. The intragrain values for the best solar cell are significantly higher than the average value of $J_{sc,avg}$ = 38.7mA/cm² extracted from a complete cell analysis.

The next development step for adapting the TOPCon approach to n-type HP mc-Si material is an optimization of the boron emitter diffusion in combination with an advanced texturing process; this is expected to significantly increase the overall current density J_{sc}. Additional process steps, such as phosphorus diffusion gettering and adapted hydrogenation for defect passivation, may help to reduce even further the bulk recombination, especially at the grain boundaries, thus reducing the losses directly attributed to the bulk material properties. An optimal implementation of these prospective improvements would result in an overall cell efficiency of the order of 22% [7].

"The creation of the first solar cells with efficiencies of up to 19.6% corroborates the potential of this new material development for high-efficiency solar cells on multicrystalline silicon wafers."

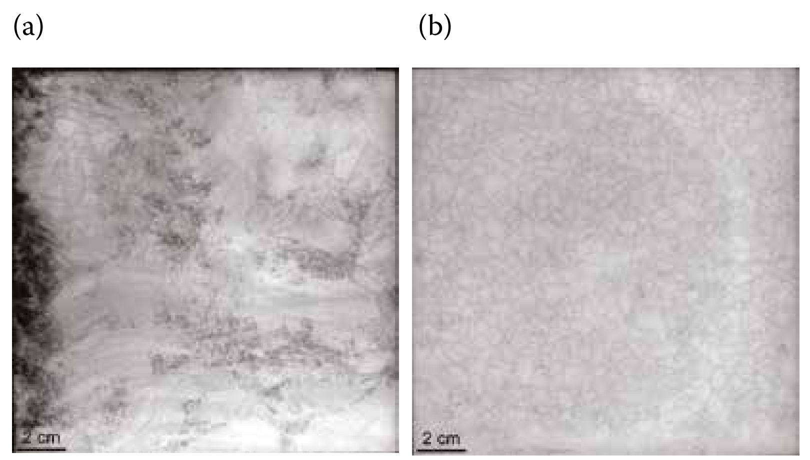

Figure 6. PL image of a wafer from (a) a standard mc-Si edge brick and (b) a HP mc-Si centre brick. The difference in material homogeneity with respect to grain size and the widely differing number of dislocation networks (tangles) are clearly visible.

Conclusion and outlook

On the road to achieving highly efficient solar cells, the development of n-type high-performance multicrystalline silicon has been proved to be a promising option for reducing bulk material limitations for cast silicon ingots. With the use of granular silicon as seed material, n-type multicrystalline wafers with significantly reduced numbers of dislocations and subgrain boundaries can be produced. When an advanced solidification crucible to reduce the incorporation of impurities is employed, high diffusion lengths of up to 1,400μm inside larger grains are achieved. All this, in combination with the discussed TOPCon process, has led to the creation of the first solar cells with efficiencies of up to 19.6%, which corroborates the potential of this new material development for high-efficiency solar cells on multicrystalline silicon wafers.

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Solar cell parameters	Best solar cell (DARC)
V_{oc} [mV]	663.7
J_{sc} [mA/cm^2]	38.87
FF [%]	75.9
η [%]	19.6

Table 1. Solar cell results for the best n-type HP mc-Si TOPCon solar cell [7].

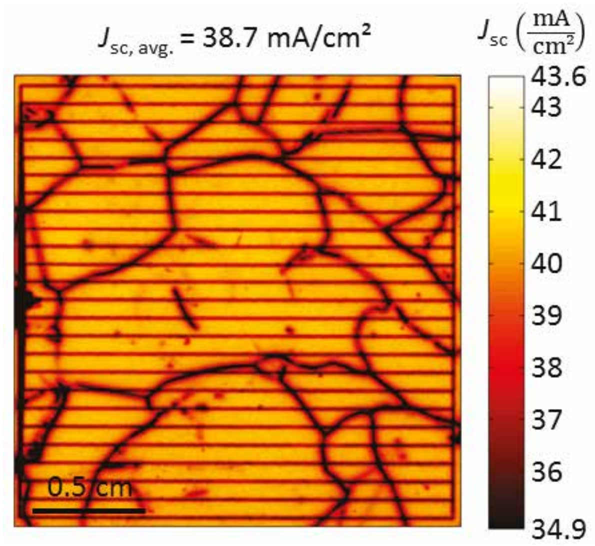

Figure 7. Spatially resolved J_{sc} map of the best solar cell with an average $J_{sc,avg}$ of 38.7mA/cm^2 [7]. (Source: Schindler et al. [7])

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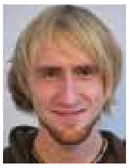

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