Presented at the 24th European PV Solar Energy Conference and Exhibition, 21-25 September 2009, Hamburg, Germany

MECHANICAL CHARACTERIZATION OF WAFER EQUIVALENT SUBSTRATE MATERIALS FROM ALTERNATIVE SILICON FEEDSTOCK

T. Orellana Pérez[1], Claudia Schmid[1], Stephan Riepe[1], Prof. H. J. Möller[2], Stefan Reber[1]
[1]Fraunhofer Institute for Solar Energy Systems ISE
Heidenhofstrasse 2, 79110 Freiburg in Breisgau
Phone +49 761 4588 5642, Fax +49 761 4588 9579, e-mail: teresa.orellana@ise.fraunhofer.de
[2]Institute for Experimental Physics and Institute for Applied Physics, TU Bergakademie Freiberg
Leipzigerstrasse 23, D-09599 Freiberg

ABSTRACT: The epitaxial wafer equivalent concept promises to reduce the cost for photovoltaic conversion. For this purpose, less expensive substrate silicon materials are used as a mechanical support for the epitaxial cell. In the presented paper the mechanical strength of different substrate materials was researched. The investigation of mechanical strength was performed depending on the relative ingot height in order to investigate the influence of contaminants and dopants segregation. The materials were tested with the ring on ring bending test. To interpret the results optical microscopy an impurity concentration measurements were done on selected wafers. It could be shown that impurities and dopants have a strong influence on the final material microstructure and thus on the mechanical strength. An increase in mechanical strength was found in certain parts of a highly Boron doped mc-Si block. Up-graded metallurgical Silicon showed less mechanical strength than industrial standard mc-Si. The quantity and the distribution of metallic impurities, mainly Aluminium, had a decisive influence on the mechanical strength of up-graded metallurgical Silicon.
Keywords: mechanical strength, crystallization, thin film, c-Si

1 INTRODUCTION

SIMTEC laboratory (Silicon Materials Technology and Evaluation Centre) at Fraunhofer ISE is currently working on the epitaxial wafer equivalent concept (Epi-Cell) for the establishment of more inexpensive solar cells. The epitaxial wafer equivalent consists of depositing an approximately 20 µm crystalline Silicon thin film by CVD process on a low cost Silicon substrate [1]. Alternative Silicon feedstock for manufacturing low cost substrates is being presently studied at SIMTEC.

The substrate provides a good mechanical strength while the epitaxial layer is responsible for the electrical performance of the final solar cell. Using Silicon as a substrate reduces problems arising from differences in thermal expansion coefficients and misfit of lattice parameters between the substrate and the thin epitaxial layer. Highly Boron doped Silicon and up-graded metallurgical Silicon (UMG-Si) can be used for manufacturing the substrate, thus saving the costs for high purity Silicon material.

The mechanical strength of the substrate material is of high relevance for the wafer equivalent and subsequent solar cell processing. Only by ensuring high process yield and mechanical strength, can the Epi-Cell concept benefit from the reduction of the overall production cost due to the use of low cost Silicon feedstock.

2 EXPERIMENTAL PROCEDURE

2.1 Wafer production and preparation

The wafers tested in the present work were provided from three multi-crystalline Silicon blocks of different material qualities which were crystallized at SIMTEC (see Table I). The crystallization variant performed was the Vertical Gradient Freeze method.

Two different qualities of UMG-Si were selected for crystallizations 2 and 3. The UMG-Si used in crystallization 3 was cleaner than the one used in crystallization 2. However, it contained a higher amount of Aluminium (Al) and the amount of crystallized Silicon was half of the amount of the Silicon in crystallization 2. Therefore, the influence of the possible incorporation of impurities from the coating of the crucible may be more noticeable in crystallization 3.

The composition of the coating is Silicon nitride (Si_3N_4) and oxygen (O_2) with a thin layer of Silicon dioxide (SiO_2) on it [2].

Table I: Type and amount of material used for every crystallization

	Material	Amount [Kg]
Cryst. 1	Cz-Si Boron doped	84
Cryst. 2	UMG-Si (99.97%)	82
Cryst. 3	UMG-Si (4-5N+1500 ppm Al)	40

156x156 mm² mc-Si ingots were cut from all blocks and sliced with the multi-wire slurry saw into 270 µm thick wafers with the same cutting parameters. Wafers from the top, the middle and the bottom part of the ingots were selected for mechanical characterization since microstructure differences due to impurities and dopant segregation are expected mainly in these areas.

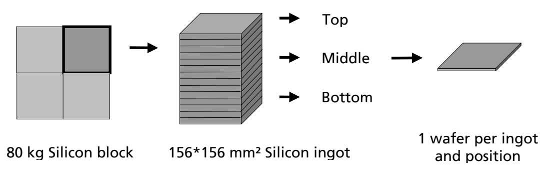


Figure 1: Scheme of the collection of wafers for the breaking test.

Additionally, one Cz-Si ingot and one industrial standard mc-Si ingot were sliced into 270 µm thick wafers to enable the comparison of the mechanical strength of alternative Silicon feedstock with solar-grade Silicon as reference.

As the mechanical strength of Silicon is just intended to be tested depending on the material quality and not on the sub-surface damage introduced by the multi-wire sawing process, the wafers were etched with a CP33 chemical solution for 2 min. A Silicon layer of approximately 12-15 µm per side of the wafer was etched in order to get rid of any sub-surface damage.

After chemical etching, the wafers were diced with a laser into 49 round Silicon chips with 22 mm diameter (see Figure 2). These chips were broken then with a ring on ring bending test configuration.

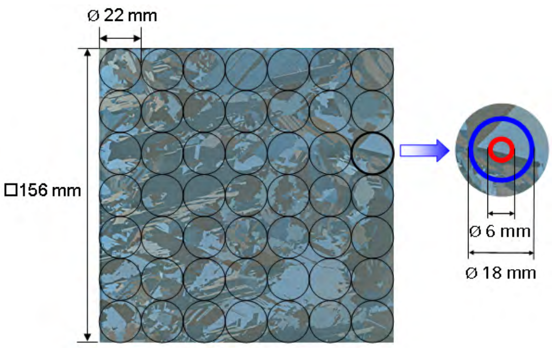


Figure 2: Sketch of the dicing of the wafers into small round chips. The dimensions of the load ring and the support ring are depicted in red and blue respectively.

2.2 Mechanical characterization

The material testing machine DO-FB0.5TS from the Zwick/Roell Company was used in the present work with a ring on ring test configuration. Since the edges of the wafers are not loaded in this configuration, this method was chosen for breaking the wafers and testing the mechanical strength of Silicon. The ring on ring bending supports were manufactured by the Zwick/Roell Company under the specifications of the ASTM C 1499 standard [3].

Figure 3: Ring on ring bending test for evaluating the mechanical strength of Silicon chips.

There were two main reasons for the selection of such a small ring on ring test configuration. The first reason is that the properties of mc-Si change according to the height of the ingot. By breaking round small chips coming from one wafer, enough samples are provided to test the mechanical strength of the material per position in the block. Also a great quantity of wafers can be saved for other purposes. The second reason is that we obtain very complete information about the mechanical strength of the wafer as bigger configurations for breaking a whole wafer may leave more amount of material without loading.

The equibiaxial bending stress at which the wafers broke under the ring on ring test configuration was calculated using the equation recommended in the ASTM 1499 standard.

$$\sigma_f = \frac{3F}{2\pi h^2}\left[(1-\upsilon)\frac{D_S^2 - D_L^2}{2D^2} + (1+\upsilon)\ln\frac{D_S}{D_L}\right] \qquad \textbf{Eq. 1}$$

F = breaking load [N]
h = wafer thickness [mm]
υ = Poisson´s ratio (0,2 for Silicon)
D_s = support ring diameter [mm]
D_L = load ring diameter [mm]
D = sample diameter [mm]

Finally, a two parameter Weibull distribution was fitted to these values by means of the maximum likelihood method. Results were depicted in a Weibull plot predicting fracture probability against applied equibiaxial stress. The following equation shows the two parameter Weibull function:

$$S(\sigma) = 1 - \exp\left(-\frac{\sigma}{\sigma_\theta}\right)^m \qquad \textbf{Eq. 2}$$

S(σ) is the fracture probability of the wafer under an applied load σ. The parameter m is the so-called Weibull modulus and describes the distribution of defect lengths. A high value of m means that the defect lengths and thus the failure stresses of the tested wafers are within a narrow scattering band; small m values indicate a broad distribution. σ_θ is the characteristic stress of the wafers which is given as the load level at which 63% of a set of comparable wafers failed [4]. The characteristic stress is considered to be a representative value for the mechanical strength of the group of samples tested.

2.3 Elemental analysis

Samples from various heights in the ingots were prepared for analysis of dopant concentration and impurity contents. For each height, samples of 10x20mm^2 sizes were cut out and analysed by GDMS (Glow-discharge mass spectrometry) for dopant and metal concentration and by IGA (Instrumental Gas Analysis) for the determination of the total Oxygen content [5].

3 RESULTS

3.1 Industrial standard Cz- and mc-Si

The comparison of Cz-Si with mc-Si reveals that the presence of grain boundaries and twins decreases the mechanical strength of Silicon. The characteristic stress of Cz- and mc-Si obtained by breaking the Silicon chips with our ring on ring test configuration is 1145 MPa and 679 MPa respectively (notice the black arrows in Figure 4). Therefore, industrial standard mc-Si is 41% less resistant than Cz-Si.

The Silicon chips were attached to a flexible polymer film on the side of the wafer under compression by a light gluing substance. As crack propagation starts in the side of the wafer under traction, the breaking behaviour is not disturbed by the attached film during bending. This way all the pieces from the Silicon chips remained together after breaking which helped to perform fractography for finding fracture origins.

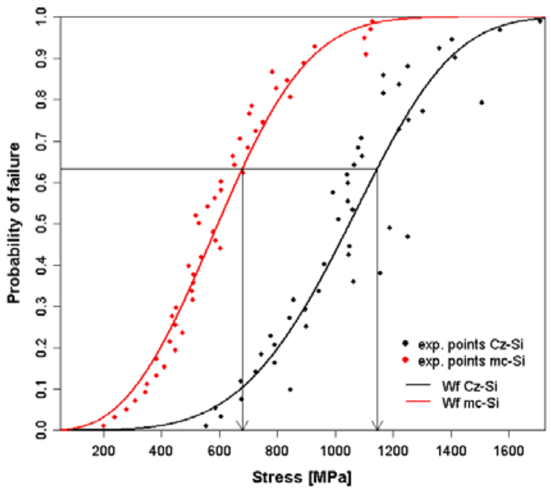
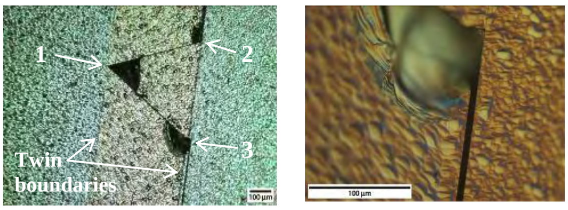


Figure 4: Weibull graph plotting failure (fracture) probability against applied equibiaxial stress for solar-grade Cz- and mc-Si wafers. The intersections of the horizontal line with the Weibull functions indicate the values of characteristic stress.

Observations of the broken side of the wafer under traction with an optical microscope pointed at fracture origins within grains, but also very frequently at grain boundaries and twins. Therefore, such crystal defects represent critical areas where fracture initiates by crack propagation (see Figure 5).



(a) (b)

Figure 5: Image (a) shows locations in mc-Si where little pieces of materials are missing due to crack propagation at twin boundaries (points 1-3). When a crack reaches the side of the wafer under compression cleavage occurs through certain preferred crystallographic planes [6]. Image (b) is a detail of the area marked in point 3 of image (a). When the crack reached the surface of the wafer under compression cleavage occurred parallel to the twin boundary.

3.2 Highly Boron doped mc-Si

The mc-Si block from crystallization 1 showed very high levels of Boron and Oxygen (see Figure 6). Whereas the total Boron concentration increases with height (as expected from segregation theory) the Oxygen content decreases. In the sample of the middle of the ingot an unexpected high value of Oxygen was found.

Relating these results with the measured mechanical strength (see Figure 7) it can be seen that segregation phenomenon in mc-Si casting really has a very noticeable impact on the mechanical properties of mc-Si.

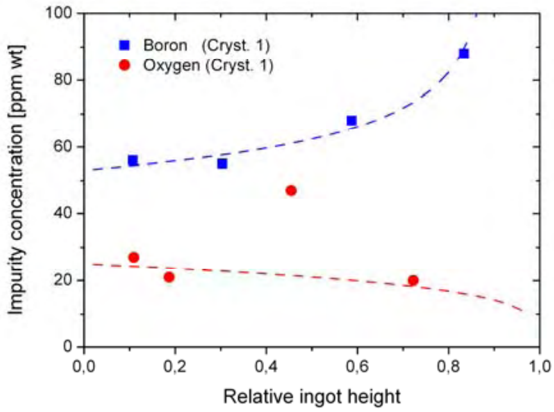


Figure 6: Distribution of Boron and Oxygen in block 1 against the relative ingot height. The dashed lines are used as guide to the eye.

The middle part of the ingot appeared to be most resistant (800 MPa) while the mechanical strength of the top part was only 587 MPa (notice the black arrows pointing at the values of characteristic stress in Figure 7). The mechanical strength of the bottom part of the ingot (704 MPa) was slightly higher than the mechanical strength of industrial standard mc-Si.

The fact that a high concentration of Oxygen was found in the middle of the block could be linked with the high mechanical strength of the wafers from the middle part. However, the measurement of Oxygen content was local and should be tested in sister wafers in order to confirm this statement.

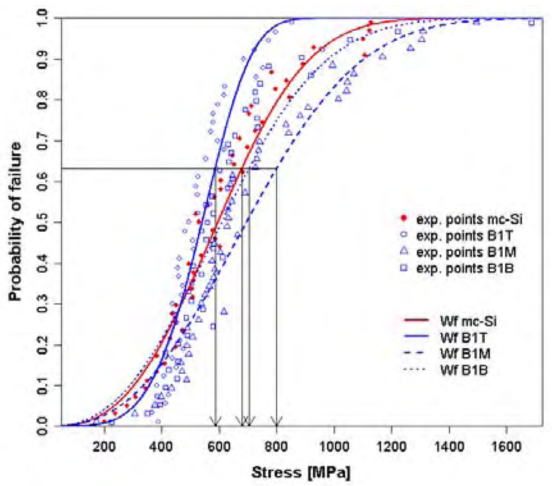


Figure 7: Weibull graph plotting failure (fracture) probability against applied equibiaxial stress for highly Boron doped mc-Si obtained in crystallization 1. The

relative positions in the ingot "top", "middle" and "bottom" are designated with the letters "T", "M" and "B" respectively.

Precipitation distribution through the height of the ingot has been analyzed with the optical microscope after polishing and SECCO etching of certain samples. Image (a) of Figure 8 reveals the presence of many and very small precipitates at the bottom of the block. In the middle part of the block there are also many precipitates but of bigger size (notice the spots in image (b) of Figure 8). At the top of the block only few big precipitates were observed. The precipitates were randomly distributed in the Silicon matrix but some precipitates alignments could also be detected (see image (d) of Figure 8).

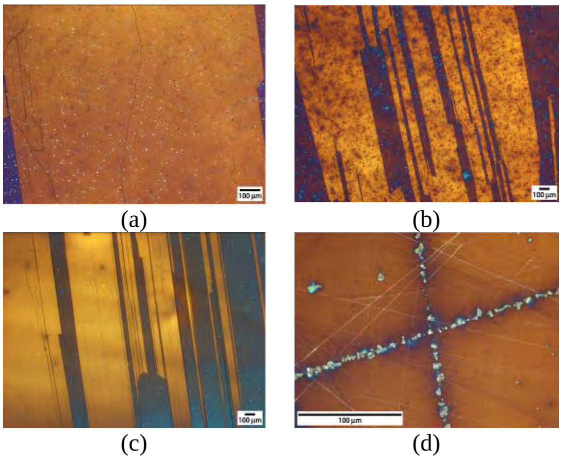


Figure 8: Distribution of precipitates in the mc-Si block obtained in crystallization 1. Image (a) shows a piece of wafer from the bottom of the ingot; image (b) corresponds to a piece of wafer from the middle of the block and image (c) depicts a piece of wafer from the top of the block. Image (d) shows alignment of precipitates very near the top of the block.

3.3 Up-graded metallurgical mc-Si

The elemental analysis for crystallizations 2 and 3 showed values below 3 ppm wt of Aluminium in block 2, but very high values for Aluminium in block 3. The Oxygen concentrations for both blocks are in the range of 30-50 ppm wt (see Figure 9).

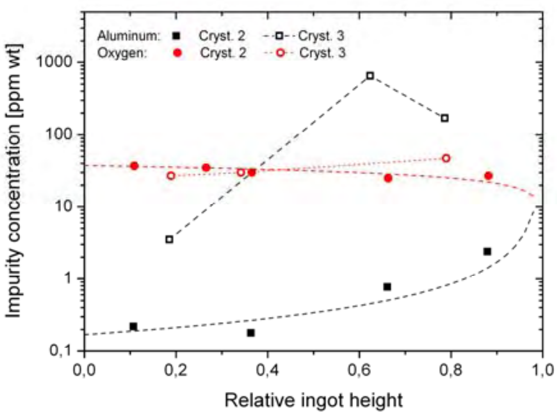


Figure 9: Distribution of Aluminium and Oxygen for crystallization 2 and 3 against the relative ingot height. The dashed lines are used as guide to the eye.

The results of the breaking tests of the material from blocks 2 and 3 confirm the dependence of the mechanical properties of Silicon on the material composition. The mechanical strength of block 2 (see Figure 10) increases in the direction "bottom to top" while in block 3 it increases in the direction "top to bottom" (see Figure 11).

The mechanical strength of the top of block 2 (713 MPa) was slightly higher than the mechanical strength of industrial standard mc-Si. The mechanical strength in both middle positions of block 2 (604 MPa and 632 MPa) was also approximate to the strength of standard mc-Si. Finally, the bottom part was the less resistant with a value of characteristic stress of 379 MPa.

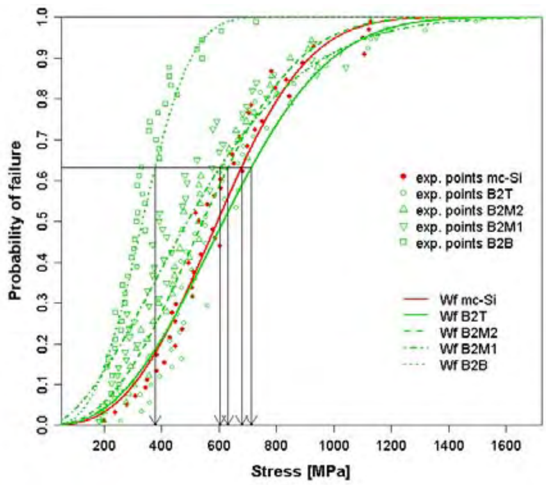


Figure 10: Weibull graph plotting failure (fracture) probability against applied equibiaxial stress for up-graded metallurgical mc-Si from crystallization 2. The relative positions in the ingot "top", "middle" and "bottom are designated with the letters "T", "M" and "B" respectively. "M2" corresponds to a middle position in the ingot nearer to the top and "M1" to a position in the ingot nearer to the bottom.

The top part of block 3 suffered a dramatic decrease in mechanical strength (100 MPa) in comparison to the strength of standard mc-Si (see Figure 11). The strength in the middle part of the block increases to 253 MPa but is still far below the standard. The bottom part of the block is the most resistant with a relatively good mechanical strength (534 MPa).

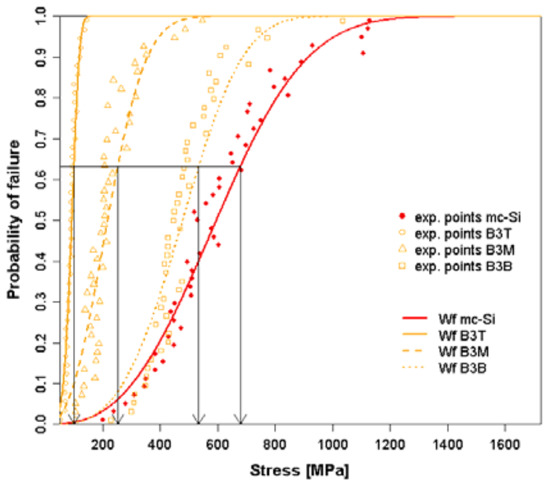


Figure 11: Weibull graph plotting failure (fracture) probability against applied equibiaxial stress for up-graded metallurgical mc-Si from crystallization 3. The relative positions in the ingot "top", "middle" and "bottom" are designated with the letters "T", "M" and "B" respectively.

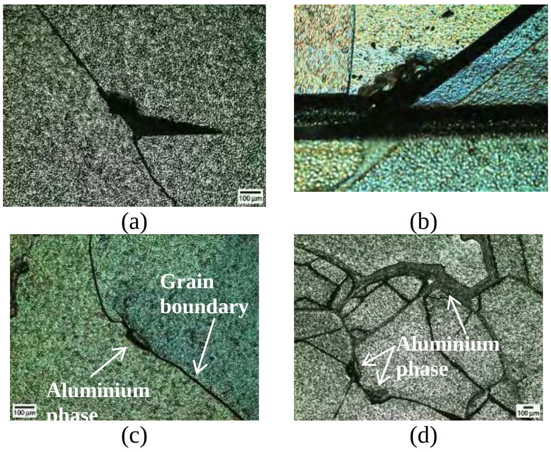


Figure 12: Image (a) shows fracture by crack propagation within a grain of a broken Silicon chip from the bottom part of block 3. Image (b) depicts fracture next to a sawing mark of a broken chip from the middle part of block 3. Images (c) and (d) show the fracture pattern in the vicinity of Aluminium phase in a broken Silicon chip from the middle and the top parts of block 3 respectively.

4 DISCUSSION

The comparison of microstructure, fracture pattern and material strength can help understanding the causes limiting the strength of the material.

In the case of block 1, fracture origins by crack propagation are observed within grains, at grain boundaries and at twins without noticing any preferred tendency. It also could be noticed that the areas which broke under crack propagation were very small and little amount of material was missing from them. Also, the fact that the parts of the block where precipitates were found are the most resistant parts, points at the phenomenon of precipitation strengthening as a possible explanation.

In block 2, grains at the top of the block are bigger and contain fewer twins than the grains at the bottom of the block. Therefore, fracture by crack propagation at grain boundaries and twins were more frequently observed at the bottom of the block than at the top. Since the mechanical strength at the top of the block was much higher than at the bottom, it can be concluded that more amount of grain boundaries and twins decreases the mechanical strength of the material.

In block 3, grains from the bottom are middle sized and show polygonal shape and some round corners. In the middle part of the ingot, the grains get sharper and elongated shapes which may indicate the presence of precipitates. Additionally, massive amounts of sawing marks on the surface of the wafers points that these precipitates most surely are SiC particles [7]. Grains at the top of the ingot show also elongated shapes. Moreover, an Aluminium phase in the top part of the block is easily visible with human eye. In this part of the block only few sawing marks were detected which points at a decrease in the precipitation of SiC particles.

Fracture pattern in the bottom of block 3 was similar to the pattern presented by other mc-Si blocks. Crack propagation was found within grains (see image (a) of Figure 12) and at grain and twin boundaries. To be noticed is that the cleavage was not always that straight as in the case of standard mc-Si but tried to take round paths trying to follow grain boundaries. In the middle part of the block, an Aluminium phase was already visible with the optical microscope (see image (c) of Figure 12). In this image the breaking path tried to follow the direction of a grain boundary. Image (d) of Figure 12 shows the breaking pattern of a Silicon chip from the top of block 3. Inter and trans-granular fracture is observed in the vicinity of the Aluminium phase. Fracture edges where not so straight and smooth as in the case of the cleaving edges of standard mc-Si.

When comparing the different qualities of UMG-Si researched in this work, it can be stated that UMG-Si from block 3 is less resistant than UMG-Si from block 2. This is due to the high content of Aluminium in block 3. Thus, we assume that the most important reason of the decrease in the mechanical strength of our UMG-Si wafers is the increasing amount of Aluminium phase with increasing height of the block.

The values of the mechanical strength of all materials tested have been summarized in the following charts. Figures 13 and 14 depict the values of Weibull modulus and characteristic stress for every block and relative ingot height. The industrial standard mc-Si is depicted in a middle relative ingot height for a correct comparison of results.

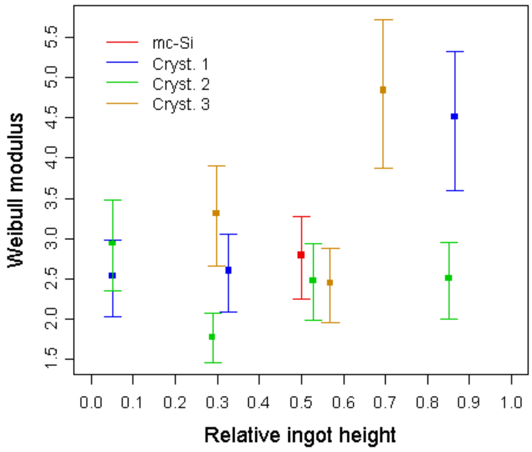


Figure 13: Values of Weibull modulus and 90% confidence bounds against relative ingot height.

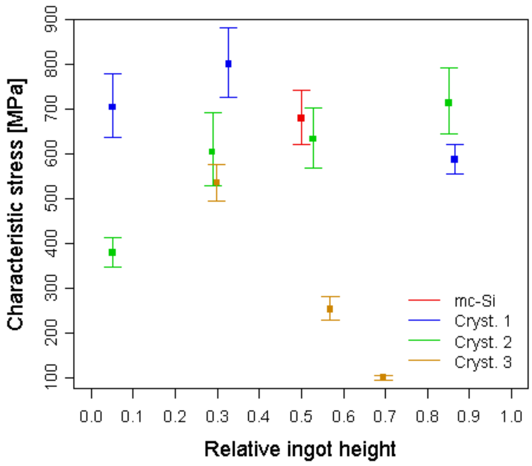


Figure 14: Values of characteristic stress and 90% confidence bounds against relative ingot height.

5 CONCLUSIONS

The comparison of the mechanical strength of mono- and multi-crystalline Silicon showed that mc-Si is 41% less resistant than Cz-Si. Thus, the presence of grain and twin boundaries decreases the mechanical properties of Silicon.

Highly Boron doped mc-Si does not show a strong deviation in its mechanical behaviour from standard industrial mc-Si; it seems to be even more resistant than standard material. The parts of the blocks where precipitates were present, especially in the middle part of the block, resulted in higher mechanical strength.

UMG-Si showed significantly worse mechanical behaviour than industrial standard mc-Si. The mechanical strength of UMG-Si has been proven to decrease with increasing contents of Aluminium as the predominant metal impurity present in the crystallized block material. Therefore, it can be concluded that impurity segregation should be controlled and optimized during crystallization in order to obtain UMG-Si with best possible mechanical properties.

6 ACKNOWLEDGEMENTS

This work has been supported by internal project funding of the Fraunhofer Society. The authors would like to thank deeply Mark Schumann, Fridolin Haas, Matthias Singh, Yaniss Wencel, Miroslawa Kwiatkowska and Martin Schwarzkopf for their support.

7 REFERENCES

[1] S. Riepe, M. Schumann, E. Schmich, S. Janz, A. Eyer, S. Reber, A. W. Bett, E. R. Weber, Proceedings 23rd European Photovoltaic Solar Energy Conference, (2008) 1264-1270

[2] R. Kvande, L. Arnberg, G. Coletti, C. Martin, C. Ndzogha, G. Rancoule, Proceedings 22nd European Photovoltaic Solar Energy Conference, (2007) 1099-1103.

[3] ASTM C 1499, “Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature”, 2008

[4] ASTM C 1239-07, “Standard Practice for Reporting Uniaxial Strength Data and Estimating Weibull Distribution Parameters for Advanced Ceramics”, 2007

[5] Evans Analytical Group, Overview Techniques & Services, www.eaglabs.com/techniques

[6] T. Orellana Pérez, K. Mayer, M. Schumann, F. Granek, Proceedings 23rd European Photovoltaic Solar Energy Conference (in press)

[7] G. Du, N. Chen, R. Prietto, Semiconductor Science and Technology, 23 (5) (2008)