New Feedstock for c-Si Photovoltaics

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Abstract. Results from functional tests of highly doped silicon purified with electron beam melting, a new feedstock for photovoltaics are presented. Possibility of obtaining dislocation free single crystals from such feedstock in typical industrial processes (CZ and FZ) is shown, crystals' parameters are tested for coherence with requirements for PV silicon.

1. Introduction
Highly doped silicon feedstock, which can be purified by means of vacuum refining, exists on the market. Electron beam melting is an energy-efficient method of vacuum refinement and in [1] we have researched its applicability for refining such feedstock. A series of experiments on new materials for crystalline silicon photovoltaics contains data on the difficulties with using such new materials, unblended with virgin polysilicon, as crystals obtained from such feedstock possess unsatisfactory physical or structural properties. The purpose of the work was to demonstrate the possibility of obtaining dislocation-free single crystals from batches with 100 percent new feedstock in typical industrial Czochralski (CZ) and float zone (FZ) processes, and to test crystals' coherence with requirements for PV silicon.

2. Experiments and results
The furnace consists of a chamber with a cooled base plate in it. A graphite crucible with a quartz crucible inside are placed on the base plate. An electron beam gun is mounted on the top of the furnace to provide heating. The scheme is provided in figure 1[1]. The appearance of the process is shown in figure 2, and the basic principle of the technology was described previously in [2].
Three different companies tested rectified material and pulled CZ monocrystals from it. Each company used its standard process of obtaining CZ monocrystals for semiconductor or photovoltaic application. Each company applied chemical treatment before pulling, and all silicon chunks were etched in a mixture of HF and HNO$_3$ to clean potential impurities off the surface. No slug or similar contaminants were found on melt surface during the process. Seeds of <100> orientation were used for pulling. In all cases, excluding company A, after initial seeding an abrupt with the monocrystal occurred before reaching the target diameter, and the initial crystal was discarded. Then, at the second attempt, full length monocrystal including the end cone, was pulled.

### 2.1. Tests in company A
Company A used a 45kg load for CZ pulling. A 16” crucible was used and crystal was pulled at 0.8-1.2mm/min rate, with the resulting diameter in the 204-210 mm range. The resulting length was 520 mm (with both cones included), and weight 38.64kg. The ingot was cut into 2 parts, of 184 mm and 223 mm. A thick (3mm) wafer was cut from each part of the ingot, wafers were annealed, then resistivity measurements were made. The lifetime was measured at the bottom of the second part, only. Results are given in table 1.

### Table 1. Resistivity, lifetime and shape of ingot parts grown at company A.

| Ingot#     | Length (mm) | Weight (kg) | Diameter (mm) | Conductivity | Resistivity ($\Omega\cdot$cm) | Lifetime (us) |
|------------|-------------|-------------|---------------|--------------|-------------------------------|---------------|
| 7-16216-1  | 184         | 14.9        | 210.2         | P            | 3.6-4.0                       | 2.7-3.0       |
| 7-16216    | 223         | 17.3        | 204-205.5     | P            | 2.8-3.0                       | 2.6-2.7       | 27-30        |

### 2.2. Tests in company B
Company B used a 60kg load for CZ pulling. After initial seeding an abrupt in the monocrystal occurred before reaching the target diameter, and the initial crystal was discarded. Then, at the second attempt, full-length monocrystal, including the end cone, was pulled. Crystal was
pulled at a rate of 0.8–1.2 mm/min, and the resulting diameter was in the 154–157 mm range. The resulting length was 1777 mm, and the weight 53.24 kg. The ingot was cut into 3 parts: of 353 mm, 356 mm and 430 mm. A thick (3 mm) wafer was cut from each part of the ingot, and wafers were annealed, then resistivity measurements were made. The lifetime and concentrations of oxygen and carbon were also measured for the top and the bottom parts. The results are given in Table 2.

Table 2. Resistivity, lifetime and concentration test results at company B.

| Measurement point (mm) | Conductivity | Resistivity at centre (Ω·cm) | RRV (%) ASTM F81 | Lifetime (µs) | N_C (10^{17} at/ccm) | N_O (10^{17} at/ccm) |
|------------------------|--------------|-----------------------------|------------------|---------------|----------------------|----------------------|
| Top (0)                | P            | >190                        | ab               | 120           | 1.0                  | 8.6                  |
| 353                    | N            | 17.8                        | 120              | a             | a                    | a                    |
| 709                    | N            | 5.5                         | 35               | a             | a                    | a                    |
| 1139                   | N            | 1.14                        | 11.6             | 12            | 9.8                  | 6.3                  |

a Not measured.

2.3. Tests in company C

Company C used a 40 kg load for CZ pulling. A Saint Gobain Quartz S.A.S. 16x12.6" crucible was used. The material underwent chemical treatment before pulling, and all silicon chunks were etched. However, a piece of quartz was found on the melt surface during the process, thus the initial crystal (shoulder and 20 mm of the body, with total weight of 1.55 kg) was discarded. Then, at the second attempt, full-length crystal, including the end cone, was pulled. The resulting diameter was in the 155–158 mm range. The resulting length was 630 mm, and the weight 33 kg (figure 3).

The path of growth ended at the 60 mm level, from the tip of the end cone at diameter ca 90 mm, dislocation withdrawal amounted to 150 mm, thus 480 mm of resulting crystal were free of dislocations. The ingot was cut into two main parts: A (diameter 154–157 mm, length 300 mm, and weight 12.08 kg) and B (diameter 157–157.5 mm, length 267 mm, and weight 13.38 kg), each of them preceded and followed by three thick wafers of 2.2, 3.0 and 3.0 thickness. The thick wafers were then annealed and used for resistance and concentrations of C and O FTIR measurements. The results of the measurements are provided in Table 3.

Table 3. Resistivity, lifetime and concentration test results at company C.

| Measurement point (mm) | Conductivity | Resistivity (Ω·cm) Before anneal | Resistivity (Ω·cm) After anneal | RRV (%) ASTM F81 Before anneal | RRV (%) ASTM F81 After anneal | FTIR measurement point (mm) | N_C (10^{17} at/ccm) Before anneal | N_C (10^{17} at/ccm) After anneal | N_O (10^{17} at/ccm) Before anneal | N_O (10^{17} at/ccm) After anneal |
|------------------------|--------------|----------------------------------|----------------------------------|--------------------------------|--------------------------------|-----------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| Shoulder (0)           | N            | P                                | 3.85                             | 7.0–7.1                        | 3.9                            | 2.2                         | 8.75                          | <0.2                           |                               |
| 316.4                  | P            | P                                | 8.83                             | 7.3–7.4                        | -4.1                           | 308.2                       | 7.62                          | <0.2                           |                               |
| 613.6                  | P            | P                                | 10.9                             | 9.5–9.6                        | -5.5                           | 589.4                       | 7.31                          | <0.2                           |                               |
| 682.6 (end cone)       | P            | a                                | 14.5                             | a                              | a                              | a                           | a                             | a                              | a                              |

a Not measured

Then glow-discharge mass spectroscopy (GDMS) measurements of CZ crystals top and end, crucible leftovers and a piece of raw material were carried out at two different laboratories. The results are shown in Table 4.
Table 4. GDMS measurements of CZ crystals top and end, crucible leftovers (potscrap) and a piece of raw material by two laboratories (concentrations given in ppbw).

| Lab | Raw material | Crystal top | Crystal end | Potscrap |
|-----|--------------|-------------|-------------|----------|
|     |              | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| [B] |              |   |   |   |   |   |   |   |   |   |   |   |
|     |              | 10 | 2 | 20 | 12 | 40 | 35 | 40 | 30 |   |   |
| [P] |              | 80 | 6 | 12 | 12 | 40 | 28 | 90 | 75 |   |   |
| [As]|              | 320 | 90 | 200 | 60 | 190 | 170 | 450 | 110 |   |   |
| [Sb]| <10          | 2 | <10 | <1 | <10 | 4-6 | 20 | 12 |   |   |
| [Ti]| 5            | <5 | 0 | 0 | <2 | 10 | 5 | 15 |   |   |
| [Fe]| <150         | 10 | <150 | 0 | <150 | 30-60 | <150 | 250 |   |   |
| [Ni]| 100          | <5 | <30 | 0 | <30 | 8 | 200 | 540 |   |   |
| [Cu]| 65           | <5 | 18 | 0 | 15 | 11 | <10 | 7 |   |   |

The tail part of the ingot was divided into four thick wafers, which were then tested for dislocations. During etching in a Sirtl bath, no dislocations were found. Only standard microdefects for CZ method (square forms as in figure 4) with density 800 per cm² appeared. Etching in a Secco bath did not reveal dislocation or square forms at <100> surface. The top part of the ingot was also tested for dislocations, and none were found.

![Figure 3. 6" crystal grown at Company C.](image1)

![Figure 4. Square forms at Si after Sirtl bath, illuminated.](image2)

2.4. Tests of FZ rods
In FZ experimental processes, two silicon rods were pulled from the crucible during the rectification process. The rods had a volatile diameter in the 100-130mm range, and weight of ca 15kg. Mechanical and then chemical treatment was used to bring rods to a constant diameter for further use in the standard FZ process. Subsequently, two FZ monocrystals, of 65 and 100 mm diameter, were grown. The resistivity and lifetime were measured at seed and non-seed ends of the crystals, and the results are given in table 5.
Table 5. Resistivity and lifetime of FZ crystals.

| Parameter         | B-3-10       | B-3-20       |
|-------------------|--------------|--------------|
|                   | Seed end     | Non-seed end | Seed end     | Non-seed end |
| Diameter (mm)     | 64-66        | 100          |
| Conductivity      | P            | P            | P            | N            |
| Resistivity (Ω*cm)  | 2.4-2.5      | 2.1-2.3      | 180          | 17           |
| Lifetime (us)     | 1780         | 1254         | 2279         | 300          |

3. Discussions

Our research [1] for individual chunks of silicon demonstrated an acceptable dopant level for further usage of the material for crystal growth. However, we have not yet performed tests on a big batch of new feedstock and dislocation-free single crystal pulling.

All growth experiments shared feedstock - heavily doped electronic grade material rectified with electron beam. Despite the fact that the same technological procedure was employed, the resistivity of the feedstock obtained varied between processes. In particular, P-type feedstock with resistivity in the 2-10 Ω*cm range was used by companies A and C and for growth of B-3-10 FZ crystal. The single crystals obtained possess acceptable uniformity in parameter distribution. The lifetime could not be measured in the crystal obtained by company C, for reasons that remain unknown.

Meanwhile, when N-type material with resistivity above 1 Ω*cm was used by company B, and high resistivity N-type feedstock was used for producing B-3-20 crystal, crystals with highly uneven distribution of resistivity along crystal length were obtained. An increase in N-type dopants' concentrations towards the end of crystal led to a decrease in the lifetime from 120 to 12 us and 2300 and 300 us, respectively.

To increase yields, the N-type dopants' content is to be minimized and the boron level is to be stabilized. To minimize the former to <10 ppba level, the dependence between dopant concentration and refinement time for the purification process needs to be found to decrease the level of impurities to an acceptable level, while keeping the process energy-efficient. To obtain crystals with resistivity in the P-type 1.5-3 Ω*cm range, boron content may be increased to a level of 70 ppbw in the existing process, but to increase yields or use this feedstock for higher resistivity applications, inner sources of boron should be found.

It is unlikely that source of boron is highly doped EG-Si, since it is produced from "virgin" polysilicon processed in CZ furnaces used for "N-processes", which implies very low levels of boron content. Quartz crucibles used for the typical CZ process generally do not introduce impurities at levels of more than 10 ppbw. Also, in previous work it has been shown that the background impurities of the rectification furnace are at level of ~1 ppbw if boron is involved.

To solve both tasks - to assuredly decrease the level of N-type dopants below 10 ppba and to prevent unsystematic introduction of boron in amounts more than 1ppbw - additional studies are necessary.

4. Conclusions

General results of this work are:

- Electron beam rectification of heavily doped electronic grade material enables one to receive feedstock that can be used directly, without blending for successful production of solar grade silicon by well-known methods such as CZ and FZ and without any modifications. These
methods, applied to the given feedstock, yield reasonable resistivity and lifetime levels in dislocation-free crystals.

- Testing of purified silicon in various independent companies showed the same results – dislocation-free single crystals were obtained without difficulties.
- The electrical parameters of ingots showed the possibility to use them for solar application.
- However, one of the key steps in obtaining material of good quality is thorough control of the initial raw material before rectification.

5. References

[1] Kravtsov A 2010 Method of vacuum refinement of silicon Russian Patent No. 2381990 (Moscow, Russia: Ruspatent)

[2] Kravtsov An and Kravtsov Al 2011 Electron Beam Silicon Purification 26th EU PVSEC (10.4229/26thEUPVSEC2011-2BV.4.7) pp 1814-1816

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