Novel method for feedstock production for high efficiency FZ c-Si PV

A Kravtsov
Scientific Director,
SIA “KEPP EU”, Riga LV-1034, Latvia
E-mail: doc@keppeu.lv

Abstract. The efficiency of solar cells manufactured from FZ wafers is significantly higher than the efficiency of cells made of CZ or multicrystalline wafers. The high cost of FZ silicon, however, limits the applicability of FZ wafers. The aim of the present work is to create a cost-effective method of FZ feedstock production based on pulling from skull with electron beam heating. This work covers the process of obtaining of raw silicon rods and FZ monocrystals from them.

1. Introduction
The efficiency of solar cells manufactured from float zone (FZ) wafers, thanks to their purity and structure perfection, is significantly higher than the efficiency of cells based on CZ or multicrystalline wafers. The applicability of such wafers is limited because of a) high depreciation costs, due to expensive FZ pullers, and b) the high price of polycrystalline silicon rods – FZ feedstock. The aim of the present work is to create a cost-effective method of FZ feedstock production. It requires crystal of cylindrical shape to be obtained from raw material applicable for PV applications, without further contamination during pulling.

2. Experiments
We based our work on an electron beam single crystals growing technique [1,2] and skull process[3]. Electron beam guns with cooled cathode were used. During the pulling process, two electron beam heaters were used. Each beam was moved over less than an 180 degrees arc with variable radius. The growth was conducted with the use of seed, which was pulled upwards while rotating. The crucible containing raw material stayed motionless. The appearance of the process is shown at figure 1.
We used leftover silicon doped by Sb and As to 100 ppm level as feedstock, then purified it prior to ingot pulling by technology described in [4]. After the purification process we pulled ingots as shown at figure 1, then we cut samples from the ends of ingots, and measured these samples by a glow-discharge mass-spectroscopy (GDMS) method. The results are shown in table 1.

**Table 1. GDMS measurements of pulled rod in comparison with undoped Si.**

|               | Undoped Si Chunk | Bottom Part of Pulled Rod |
|---------------|------------------|----------------------------|
| B             | 2.0              | 272.0                      |
| Al            | 0.7              | 1.8                        |
| Fe            | 0.4              | 0.7                        |
| Ni            | 5.2              | 0.7                        |
| Cu            | 24               | 10.0                       |
| As            | 1.0              | 1.8                        |
| Sb            | 0.5              | 1.4                        |

According to GDMS results, the purity of pulled ingots is on the same level as in standard polysilicon, except for the concentration of boron, which can’t be removed by the methods used.

A new generation of experimental furnace was created (shown at figure 2). It consists of melting and pulling (crystal) chambers, with a flap gate valve in between, a pulling mechanism and two electron beam guns, each equipped with its own power system. The process is conducted under residual pressure of not more than 0,05 mbar. The batch is placed in a copper water cooled mold, equipped with elements designed for thermal field management.
Using this equipment, we have demonstrated the possibility of manually growing crystals of diameter up to 240 mm, and the purification of heavily doped silicon in this kind of process (figure 3). However, the ingots have a very volatile diameter, so for practical application grinding should be applied to ingot surface, thus a lot of weight is lost, driving the price of feedstock to an uncompetitive level. To address this issue, we’ve organized a new activity together with Elektronikas un datozinatnu instituts (EDI) under contract with SIA “LEO PETIJUMU CENTRS” N1.1.1.-5/-7-14. The first results of this activity (actually the second process from the beginning of cooperation) yielded a much better ingot surface, shown at figure 4. Enhancement was achieved due to the employment of PID-regulation of pulling rate, where the correction to rate value was calculated solely from the deviation between crystal-melt meniscus diameter and its preset value.
**Figure 3.** Rods pulled with electron beam heating with significant diameter fluctuations to +/- 10 mm.

**Figure 4.** Silicon rod obtained with electron beam heating and enhanced diameter stabilization (with diameter fluctuation of less than +/-5 mm).

The rods obtained were tested for acceptability in FZ single crystal growth at the Leibniz Institute for Crystal Growth, Berlin, Germany (IKZ). Only one out of two rods tested yielded a small, defect-free single crystal with diameter under 80mm, shown at figure 5. In our opinion, the appearance of dislocations can be attributed to alien inclusions, described below.
Phase boundary measurements, using LPS of the rods obtained, were made in IKZ (figure 6). Measurements revealed that the crystallization front in rods pulled with the use of electron beam heating is curved towards melt (downwards) and has a substantial sag of ca 15mm for 100mm rod diameter, which can be attributed to the character of the surface heating.

**Figure 5.** Place of generation of dislocation at conical part of single crystal, grown from rod obtained on new generation of equipment.

**Figure 6.** Crystallization front shape for rods grown with electron beam heating.

### 3. Results and discussions

Since trial growth did not result in obtaining defect-free monocrystals and the crystallization front study did not reveal the source of the problem, the initial research of pulled rods was made together with LU CFI, Riga, Latvia (CFI). Raman spectroscopy and SEM studies were performed at this stage.

Raman spectroscopy (figure 7, made by CFI) was conducted on a plate-shaped silicon sample mirror, polished on both sides with the use of two spectrometers in the 200..2000cm$^{-1}$ range:
Spex Ramalog (USA) (Resolution: 1 cm⁻¹, laser line: 532 cm⁻¹);
Advantage NIR (USA) (Res.: 3 cm⁻¹, laser line 785 cm⁻¹, objective: 90x).

Surface contains monocrystalline (522 cm⁻¹ shift) and polycrystalline (517 cm⁻¹ shift) parts. Also, as yet unidentified peaks with 543 cm⁻¹ shift were observed.

Scanning electron microscopy (made by LU CFI, Riga, Latvia) revealed alien inclusions shown at figure 8. Possibly, this inclusion is silicon carbide, however, research is not finished yet and requires to be continued.

Previously, we have published [5] results where full-length, dislocation-free FZ single crystals were obtained from rods pulled in processes with a load weight less than 25kg. From our viewpoint, the difference between the results obtained for small and enlarged loads can be attributed for the most extent to the use of materials which were not previously used in a hot zone. In particular, while creating new hot zone carbon, containing materials were used, which if contacted by electron beam or molten silicon could produce SiC particles. To prevent an appearance of the alien particles described, we are making modifications in hot zone design with the use of carbon-free materials.

Figure 7. Raman-spectra for different points of silicon sample.

Figure 8. SEM analysis of silicon rods.
4. Conclusions
General results of this work are:
- An experimental furnace for pulling rods applicable in FZ process has been created.
- We successfully created the basis for technologies of:
  - production of competitive FZ feedstock from recycled materials in an arbitrary form, such as chunks, etc;
  - recycling leftovers of the FZ process.
- The possibility of manually growing crystals of diameter up to 240 mm has been revealed.
- The possibility of satisfactory diameter stabilization by means of PID-control of pulling rate, based on the measurement of the diameter of rod-melt meniscus, has been demonstrated.
- The possibility of purification of heavily doped silicon in this kind of process, has been demonstrated.
- The dislocation-free part of single crystal obtained proves the principal possibility of yielding dislocation-free single crystals from rods pulled from up to 100kg loads.
- It is necessary to proceed with working on hot zone design enhancement.

5. References
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