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Development of silicon growth techniques from melt with surface heating

Anatoly Kravtsov

KEPP EU AS, Carnikavas iela, 5, Riga, LV 1034, Latvia

E-mail doc@keppeu.lv

Abstract. The paper contains literary and personal data on the development history of silicon-growing technology with volumetric and surface melt heating. It discusses the advantages and disadvantages of surface-heating technology. Examples are given of the implementation of such processes in the 60s-70s of the last century, and the reasons for the discontinuation of the relevant work. It describes the main solutions for the implementation of crystal growth process with the electron-beam heating of the melt surface, implemented by KEPP EU (Latvia). It discusses differences in the management of the growth process for the crystals with constant diameters compared to the Czochralski method. It lists geometrical and electro-physical properties of the obtained crystals. It describes the possible use of such crystals and the immediate challenges of technology development.

1. Introduction

The historical overview of silicon crystal growth methods goes beyond the scope of this article, but in my opinion, since some historical data corroborate the ideas presented, they should be illustrated in Table 1.

Table 1. The historical overview of silicon crystal growth methods.

Tab 1. Silicon crystal growth history

Year	1950	1956	1962	1967	1972	1973	1974	1976	1980	1984	1986	1988	1990	1992
CZ diameter, mm [1]	12	25	40	50	65	78			100	125		150		200
CZ charge, kg [1]	0,05	0,4	1,2	2,5	6	12			24	38		65		110
FZ diameter, mm [2, own data]		10	40				65	78	100		125		150	
FZ/pydestal diameter [3,4]			40		42									
Skull silicon diameter,mm [5, own data]				40	45									

2. The influence of heating methods on the properties of crystals and the development of processes

The fundamental difference between the CZ (Czochralski method) and DS (direct solidification) methods from the FZ process, the pedestal growing, and the skull-melting is most vividly illustrated by the numerical simulation diagrams of these processes shown in Figure 1. The typical size of the heating zone in FZ processes and when growing by electron-beam heating is 10-30 mm. For growing methods with volumetric melt heating (CZ and DS), the typical size of the heating zone is measured in

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hundreds of millimetres, and the surface area in modern systems is about 1 square metre. It is clear that in the case of volumetric heating, the systems are characterised by more homogeneous thermal fields favourable to the growth of crystals. At the same time, a large number of different tooling mainly made of graphite used in volumetric heating methods results in inevitable contamination of the melt during the process. The absence of such a tooling in the processes of surface heating provides these methods not only with the ability to produce cleaner crystals, but also gives them some economic advantage due to the absence of the expenses for the consumable tooling.

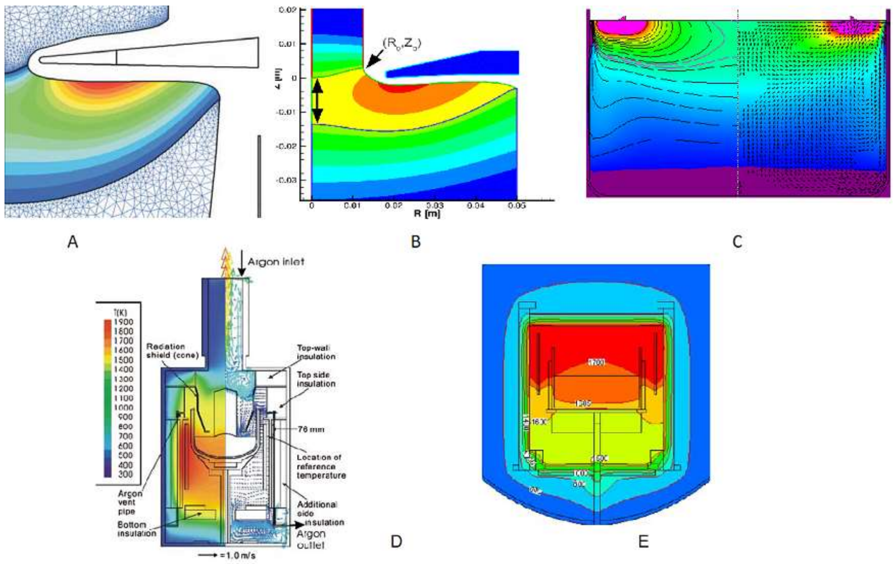

Figure 1. Area of heating in different crystal growing techniques (temperature distribution):
A- FZ [8];
B - pydestal [4];
C - Electron beam [own data];
D - CZ [9];
E – DS [10].

On the other hand, surface heating methods have a number of drawbacks.

For the FZ process and pedestal growing, a polycrystalline silicon rod is needed, corresponding to a number of specific geometry requirements - high density, and lack of cracks and amorphous phase inclusions. The fact is that the diameters of the original and growing rods should not differ by more than 20% in the standard FZ process. As for the pedestal growing process, the situation is even worse - the diameter of the growing rod is almost 2 times smaller than the pedestal diameter. The development of deposition technology for these rods in the Siemens process takes considerable time. As a result, the lack of adequate methods of obtaining rods hindered the development of the FZ process in the late 1960s, in the early 1970s, and in the early 1990s. To ensure the quality requirements for the rods, the processes of their deposition are executed at a slow rate. Compliance with this growing technology makes rods very expensive - at least twice as much as pieces of polycrystalline silicon of the relevant quality used in the process of growing from the crucible. The high price of rods causes a high price of FZ single crystals and limits their use. This leads to another problem - the complex and costly equipment for the FZ process is produced in small amounts.

The high cost of developing such equipment is allocated to a small number of produced plants and significantly increases the cost of equipment. As a result, a second significant component of the cost of FZ silicon - depreciation deductions - are added, which adds to the price and restricts the use of FZ single crystals. Savings resulting from the lack of additional consumables are insufficient to compensate for the high cost of raw materials and depreciation deductions, so it results in the use of FZ silicon being limited to special detectors and power electronics, where such silicon cannot be replaced with the cheaper one. The ever-increasing demands to energy network loads add to the requirements for plate diameter.

Given the current trend and according to the estimates [12], the need for plates of 300 mm in diameter should be expected by 2020. In order to solve this problem, firstly, it is extremely important to produce the high-purity rods of the appropriate diameter (250-350 mm), and secondly, it is necessary to reduce the voltage in the inductor to eliminate the discharges typical of the more than 2

MHz current frequency used in the FZ process. When using low frequencies, such as 1.76 MHz [11], the problems occur with the source rod melting. Thus, currently there is an interest in 300-millimetre plates for powerful thyristors, but there are no polycrystalline rods for the production of single crystals with a diameter of 300 mm and equipment for the implementation of the FZ process. However, real industrial development will require a solution in the next 5-7 years. Our goals was to create equipment and technology for the production of feeding silicon rods for FZ process of growing silicon single crystal 300 mm in diameter.

3. Growing crystals with electron beam heating

Electron-beam heating processes were used in the growth of single crystals with dislocations on a pedestal [4] in a vacuum. There are two main problems with this process: the optimal distribution of heat, and the substantial evaporation of silicon. Evaporated silicon condenses on the surface of a vacuum chamber, and then the condensate falls into the melt and enters the crystallisation surface, resulting in the stop of the crystal's monocrystalline growth. As a result, these processes have not progressed. On the other hand, several versions of the process using skull-melting were patented at different times, and their diagrams are shown in Figure 2.

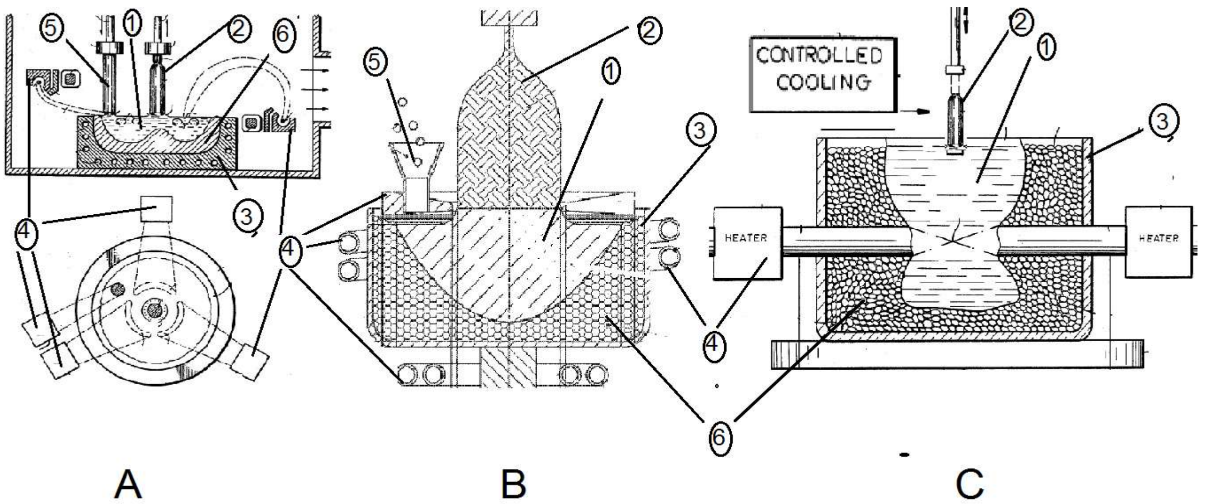

Figure 2. Different types of skull pulling processes
A–from cold crucible [5]; C–multiple induction heating [14]; B– inside electrical current heating [13]. 1- melt; 2-pulled crystal; 3-crucible; 4-heating source (A- electron beam; B- multiple induction coils; C- electrical current flow); 5- silicon source; 6 – silicon skull.

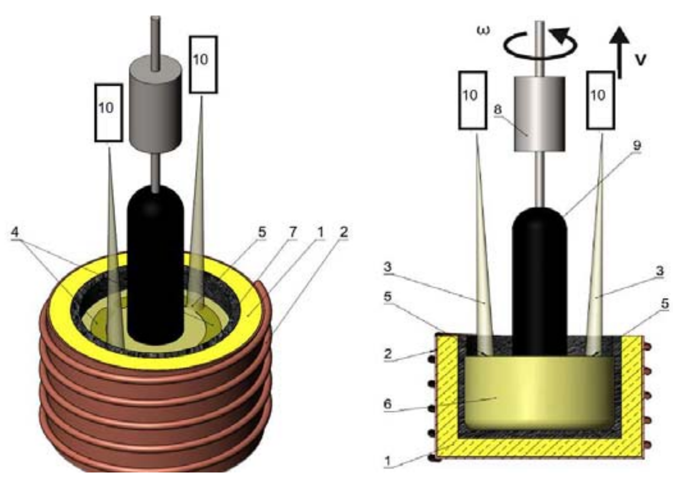

Figure 3. Electron beam pulling process developing at KEPP EU
1-cold crucible;
2- insulation;
3-electron beam;
4- way of focal spot on melt surface;
5-focal spots; 6- melt;
7- container; 8- seed holder
9 – pulling crystal;
10- electron beam gun.

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Although these diagrams have a number of drawbacks, silicon crystals have been obtained using them. The diagram in Figure 2a greatly benefits from zero requirements for the size and shape of the source material, except for the feeding rod. Obviously, the main problem with the process is the difficulty of heating up the central area of melt, which is cooled using a copper crucible and tends to attach to the growing crystal. To resolve the above problem, we developed a furnace and a process diagram with reduced heat emission from the bottom part of the melt shown in Figure 3.

Thermal insulation improves the energy efficiency of the process. In the case of the rod growth with the diameter of 200 mm, the entire process consumes up to 25 kWh/kg, including melting of the source silicon and growing of the crystal; the crystal was grown at a rate of 0.5-2 mm / min while rotating at least 10 rpm. The first crystals with a diameter of about 100 mm were obtained in 2011. In 2014, the diameter of rods grown in a stable process reached 170 mm, in 2016 it was 220 mm and 300 mm in 2017.

Figure 4. Electron beam pulling process. A- puller (detail description in [15]); B- 6”; 9”; 12” ingots archived on puller shown at A; C- view of process.

Developed equipment does not use a movable melt bath, thus eliminating the mixing of melt resulting from the crucible's rotation. The symmetry of heating is ensured by the movement of the electron beams' focal spots. However, there is a problem with the control of the crystal's diameter. As the crystal grows, the melt level decreases and the controlled meniscus moves away from the camera. The attempt to use the laser distance meter to determine the position of the melt and introduce an adjustment in the direction of the camera axis has encountered a problem of reflected rays being scattered, as there is a wave on the melt surface. This wave is the natural property of the process. The point is that the electron beam creates pressure on the surface of the melt, and as a result, the beam displacement forms a wave. In addition, the electron beam produces a glowing trail, and the melt meniscus near the skull-melting surface has almost the same brightness as the control meniscus near the growing surface of the crystal (Figure 4).

As a result, the camera periodically "loses" the monitored object. We were actually able to solve this problem [16] by filtering the images. This resulted in a programme developed to adjust the diameter by changing the speed of pulling, but the control over the melt level is not yet resolved. As a result, an industrial plant designed for growing polycrystalline rods from silicon (Figure 4a) has been developed, and the methods for growing rods with a diameter of up to 220 mm have been mastered. Also, the possibility of growing crystals with a diameter of up to 300 mm (12 inches) has been demonstrated. The maximum mass of the obtained crystals is 90 kg at 110 kg of consumed material.

The results of monitoring impurities in the grown crystals (N 3-2) and melt residues (N 5-2) compared to FZ silicon of high purity (N-HR) are shown in Figure 5.

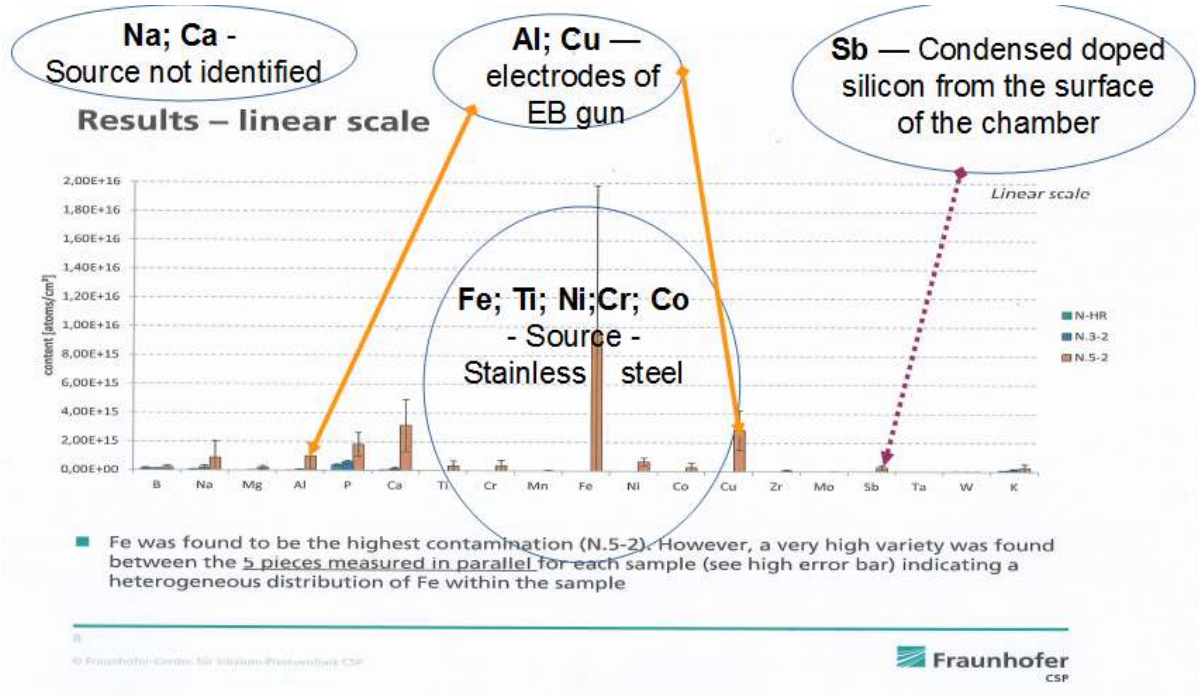

Figure 5. Results of impurities control in high resistivity FZ sample (N-HR), sample from bottom part of electron beam pulled rod (EBR) (N 3-2) and residues of melt (N 5-2).

4. Increasing the purity of silicon grown using electron beam heating

Within the capabilities of ICP MS, it has been demonstrated that the resulting purity of the rod (sample No. 3-2) is almost the same as the purity of the high-purity reference sample of FZ silicon (N-HR). The analysis of detected impurities indicates the need to clean the surface of the vacuum chamber before the process of obtaining pure rods, and to form and maintain a condensed pure layer of silicon on them. The formation of a group of metallic impurities similar to stainless steel by composition indicates that the surfaces of the vacuum chamber and other steel parts are dispersed when irradiated by the primary or secondary electrons. The most dangerous surfaces are those that can be irradiated by primary electrons with trajectories slightly deflected from the main flow axis. Because of the relatively small number of such electrons, they do not leave traces on steel surfaces but result in saturation of residual gases with metal vapours in the vacuum chamber. Another source of contamination is the electron-beam heater electrodes. In order to prevent electrode materials from entering the melt, a gas-dynamic window was developed to separate the heater's gas-discharge chamber from the plant's processing chamber. On the side of the processing chamber, an inert gas is fed to the membrane, and on the side of the gas-discharge chamber, a zone of increased pressure is created for a mixture of this inert gas with gases that initiate plasma and contain vapours of electrode materials. Along with the electrode materials, the gas mixture is removed from the high-pressure zone by an additional vacuum pump.

5. Conclusions

1) The advantages and disadvantages of silicon crystal growth technology using local surface heating are analysed.

2) The world's first equipment and technology have been developed, allowing to ensure the growth of silicon rods from the melt heated by the electron beam. An example of methods of obtaining polycrystalline rods with a diameter of up to 300 mm suitable for growing single crystals in the FZ

process is provided. The purity of rods monitored at the level of the MS ICP method corresponds to the purity of the standard FZ silicon.

3) Sources of impurities entering the melt during the process of growing have been identified, detected by analysing the traces in the melt residues left after the growing process. Ways of eliminating these sources to improve the quality of the grown rods have been designated.

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References

[1] Werner Zulehner, 3 April 2000, Historical overview of Silicon crystal pulling development. *Materials Science and Engineering*: B, Vol. 73, Issues 1–3, pp 7-15
[2] Ratnieks G., 2007, Modelling of the Floating Zone Growth of Silicon Single Crystals with Diameter up to 8 Inch. Ph.D. Thesis.University of Latvia Faculty of Physics and Mathematics Department of Physics, 176
[3] Ciszek T F, 1972, Growth of 40 mm diameter single crystals by a pedestal technique using electron beam heating, *Journal of crystal growth*, No. 12, pp 281-287
[4] Wünscher M, Riemann H, Hallmann-Seifert B, Lüdge A, March 23-30 2011, Crucible-free Crystal Pulling of Germanium Scientific Seminar on Application of Germanium Detectors in Fundamental Research Tsinghua University, Beijing/China
[5] Charles W H, Charles D A H, 1968, Method for growing crystals, Patent US 3494804 A Continuation-impart of application Ser. No. 659
[6] Schmid F, 2013, History of Technologies, development for Solar Silicon Cost Reduction, Solar Power for the World What You Wanted to Know about Photovoltaics Wolfgang Palz Pan Stanford Publishing, pp 257–274
[7] Jinggong, Science & Technology Co., Ltd.: http://www.machingservices.com/polysilicon-casting-furnace-manufacturing-products.html
[8] Muižnieks A, Rudevičs A, Krauze A, Suškovs V, Surovovs K, Janisels K, Mathematical modelling of silicon single crystal industrial growth, https://www.lu.lv/fileadmin/user_upload/lu_portal/projekti/atom/Muiznieks.pdf
[9] Chung-Wen L, Chao-Kuan H and Wen-Chin H, 2009, Czochralski Silicon Crystal Growth for Photovoltaic Applications, *Crystal Growth of Silicon for Solar Cells,* XIV, 255, pp 25-39
[10] Wei J, Zhang H, Zheng L, Wang C, Zhao B, 2009, Modeling and improvement of silicon ingot directional solidification for industrial production systems, *Solar Energy Materials & Solar Cells* 93, 1531–1539
[11] Menzel R, 2013, Growth Conditions for Large Diameter FZ Si Single Crystals von der Fakultät II – Mathematik und Naturwissenschaften der Technischen Universität Berlin zur Erlangung des akademischen Grades genehmigte Dissertation Dr. Ing. Berlin, p 101
[12] Deboy G, Aigner K, 2013, Power Semiconductors on 300-Millimeter Wafers, *Semiconductors*, Issue 3, Power Electronics Europe, pp 44-47
[13] Pinkhasov E, Vernon Mt, 1984, Method of and apparatus for the drawing of bars monocrystalline silicon, United States Patent 4,575,401 Flled: Int. c1.4 c301; 15/14 US. Cl.. 156/602; 156/617 M
[14] Riemann H, Abrosimov N V, Fischer J, Renner B M, Wusterhausen K, 2010, Method and apparatus for producing single crystals composed of semiconductor material, *US Patent Application Publication* (10) Pub. No.: US 2012/0285369 A1 Filed: Int. Cl. C30B 15/14 (2006.01) C30B 15/02 (2006.01) (52) U.S. Cl. 117/13; 117/214

[15] Kravtsov A, 2014, Ingots Pulled with Electron Beam Heating from Skull a New Feedstock for FZ Crystals Applicable for Solar Cells, in IEEE PVSC40, Denver, CO, USA
[16] Kravtsov An, Kravtsov Al, Fuksis R and Pudzs M, 2015, Ingot pulling with electron beam heating: Process enhancements, *Photovoltaic Specialist Conference (PVSC)*, IEEE 42nd, New Orleans, LA, pp 1-4