

Upgrading Metallurgical Grade Silicon to Solar Grade Silicon

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Abstract

The photovoltaics (PV) is a method of direct conversion of solar energy to electricity using semiconductor solar cells. In terms of globally installed capacity, PV remains third the most important renewable energy source after hydro and wind powers. 31.1 GW of PV systems were installed around the world in 2012 and up from 30.4 GW in 2011. There is a rapid growth of PV cell production and it is expected to increase further. However PV technology have to cost effective in comparison to hydro or wind powers and other sources of renewable energy. It has to reach the “grid parity” i.e. less or equal price for generated electricity power. More than 85% of solar cells (SC) are made from solar grade silicon (SoGSi). SoGSi is produced by purification of metallurgy grade silicon (MGSi) which is produced by carbon recovering silicon from quartz. Also Quartz is an initial and essential material for obtaining SoGSi and SC. Rich resource of quartz Sarykol located at southern part of Kazakhstan where the main factory for MG Si production «Kazsilicon» is situated. Upgrading of MGSi up to SoGSi consists is a number of technological steps and SoGSi is basis for PV industry. Therefore the cost of SoGSi determines the competitiveness of PV technology compared to other energy sources. There are several chemical and metallurgical technologies for SoGSi production. This paper briefly describes these technologies and shows main advantages of metallurgical technologies based on slag refining (oxygenation). Considered technologies are the basis for industrial production of SoGSi, solar cells with an efficiency of 15.8-17.1% and solar panels. The 1st power plant made from solar panels in Kazakhstan was launched in December 25, 2012 by «AstanaSolar» with a total capacity of 250 kW.

Introduction

Sun as an energy source makes solar energy conversion technology increasingly important. Thus the demand for solar cells, which convert sun light directly into electricity, is growing. Solar or photovoltaic (PV) cells are made up of semiconductor materials that absorb photons from solar light and then release electrons, causing generation of electricity. According to the EPIA's data, worldwide installation of PV systems reached 31.1 GW in 2012 and up to 30.4 GW in 2011. After hydro and wind powers, the PV remains third the most important renewable energy source in terms of globally installed capacity. The strong growth in PV cell production is expected to continue further [1]. Silicon is the most suitable material for industry scale solar cells, it is safe and one of the most abundant resources on Earth, repre-

senting 26% of crustal material. The abundance and safety of silicon as a resource provides the crystalline silicon solar cell a prominent position among all the various kinds of solar cells in the present and future PV market [2, 3]. World annual PV cell production of more than 100 GW is expected to be achieved by around 2020 and the silicon PV cell is the most real candidate to meet this demand from the point of view of suitability for large-scale production. Therefore PV's rapid growth must be provided by huge production of low cost solar grade silicon (SoGSi) feedstock [2-4]. There are two main kinds of Si feedstock. The first one is electronic grade silicon (EGSi) produced by chemical methods based on Simmens and Union Carbide processes [5]. Another one is based on alternatively upgraded Si – also called “upgraded metallurgical-grade” or UMG silicon. Initial material for UMG technology

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is MGSi with a purity of 98-99%, typically. Metallurgical refinement for gaining UMG-Si has the obvious advantage of staying in the liquid phase of Si, resulting in an extremely important advantage in comparison to EGSi production and derivatives: less energy consumption. Elkem Solar was the first who suggested metallurgical refining route to produce SoGSi and SC from MG silicon in 2009 and succeed in it [6]. In spite of the differences in terms of technology from the conventional feedstock of polysilicon, the SC efficiencies made from UMG-Si are comparable to SC made from SoGSi obtained by chemical methods. Not only there is an additional benefit of lowering specific energy use, i.e. reduced cost per kWh, but it is more environmentally friendly too. These advantages come at the cost of lower Si purity levels (ppm range). Within less than 10 years we have seen a tremendous quality improvement of refined metallurgical UMG-Si, along with a trend of merging characteristics when comparing respective producers, most of all in terms of concentration levels and ratios of the dopant elements, boron (B) and phosphorous (P). B and P simultaneously present as inherent contaminants and thereby leading to a compensated state of such Si. Also the impact of compensation on critical cell properties is not yet fully understood, similar to the required purity level mentioned above. KazPV project is dedicated to organization of PV industry in Kazakhstan based on MGSi plant produced at Ushtobe by «Kazsilicon» and technology transfer for upgrading [7]. This MGSi – relatively cheap metallurgical grade silicon is the starting material for getting SoGSi and SC as well and Sarykol's quartz is an initial material for obtaining MGSi. Sarykol is huge, 1.7 million tons deposit of high purity quartz, located at South part of Kazakhstan where «Kazsilicon» is placed. It is the main factory for MG production in Kazakhstan.

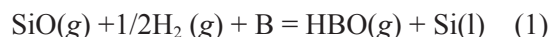
This paper presents the results of studying of upgrading MGSi up to SoGSi by slag refining method in the framework of KazPV project.

Results and Discussions

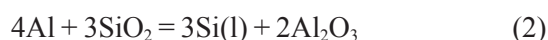
The main steps of Kazsilicon carbothermal process have been considered before [4, 5, 7] and Fig. 1 illustrates both boron and phosphorus contents in obtained MG-Si.

However for utilization of MGSi as SoGSi, must be purified up to level 99.9999 percent, 6N pure for production of silicon solar cells, which are main devices for PV modules. Nowadays, one of the most promising and commonly used methods for purification of MGSi up to UMGSi and up to SoGSi is the oxidation or slag refining [4, 6-11]. Removal of impurities from liquid silicon requires oxidation

to form an impurity species and partitioning of this species from liquid silicon into a second phase. For example (1), boron reacts to form HBO(g) and is removed from liquid silicon by partitioning to the vapour phase.



Part of impurities such as Al, Ca, and Mg can also get partitioned during oxidation into a liquid phase such as a slag (2) to (4) or into a solid phase like as SiO₂ (5).



Several groups [3, 4, 6-11] have implemented an industry scale refining of MGSi up to SoGSi. However every approaches has its know-how procedures. The purification methods of MG Si have been worked out by «Kazsilicon» in the framework of KazPV project.

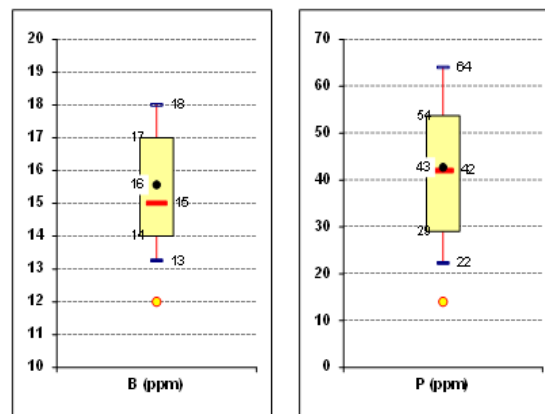


Fig. 1. Statistical charts for one month of boron and phosphorus contents in Kazsilicon MGSi. Average values of boron is 16 ppm(w) and phosphorus is 43 ppm(w).

KazPV project is an advanced industrial pilot line in Kazakhstan for 60MW photovoltaic (PV) production based on local solar grade silicon (SOG-Si) manufacture. Important point of project is the completely vertically integrated process, starting from high purity quartz (HPQ) and carbon selection for the reduction of metallurgy grade silicon (MG-Si) and finishing with a production of solar panels at competitive level. Figure 2 displays the main steps of KazPV project.

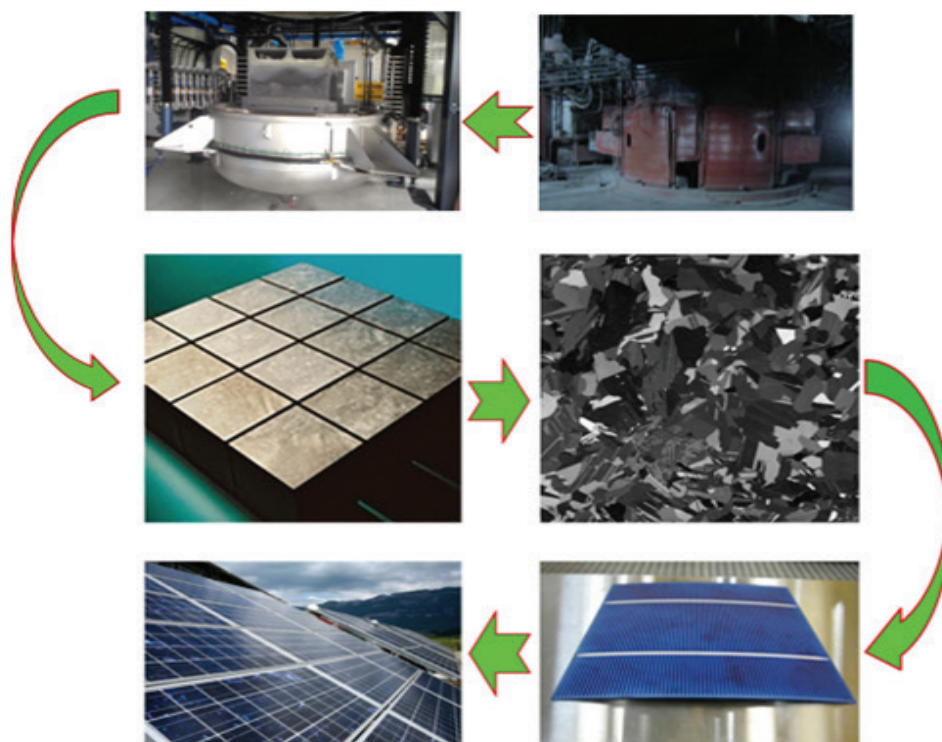


Fig. 2. KazPV project technological steps to obtain photovoltaic panels.

Following production line includes next steps:

- MG Si production using electric-arc ore-thermal furnaces. Technical characteristics of the furnace are indicated in Table 1.
- Purification of MGSi to SoGSi via metallurgical refinement methods, i.e. slag refining, acid leaching, directional solidification and production of polycrystalline silicon ingots.
- Sawing of ingots into blocks with a square section that determines the future shape of photovoltaic cells.
- Sawing of the polycrystalline silicon based blocks into wafers on special saws using the slurry composed of polyethylene glycol (PEG) and silicon carbide particles.
- Production of cells from wafers using texturization, phosphorus diffusion, application of antireflection coating, screen printing and contacts heating.
- PV modules assembly.

The blocks obtained after sawing the ingots are tested using infrared radiation. This analysis grants a contactless method for easy and fast diagnosis of the blocks for any defects such as cracks, voids, inclusions of various kinds, as well as a view on the direction of growth of crystal groups. Figure 3 includes photos of five silicon blocks in infrared light. as seen on photos there are no silicon carbide and silicon nitride inclusions, as well as any other physical defects, which is an indicator of high quality of material and technology used for ingot production.

Table 1
Specifications of Kazsiliko's furnace
for MGSi production

Title	Units	Amount
The furnace power	kW	9600
Graphite electrodes diameter	mm	610
Number of electrodes		3
The diameter of the furnace bath	mm	4200
Furnace bath depth	mm	1750
daily productivity	ton	15
Annual output	ton	5000
Electricity consumption (per 1t of silicon)	kW	12500
Quartz consumption (per 1t of silicon)	ton	2.7
MG-Si quality after refining: using technology option I	% Si	99.3-99.6%
using technology option II		99.6-99.9%

Lifetime of minority carriers is one of the most important quality parameters of the material used for manufacturing of silicon based PV cells. Figure 4 illustrates a map of lifetime distribution of polycrystalline silicon block's cross-section. 5.5 microseconds is the average lifetime of minority carriers of polycrystalline silicon block that is produced using Kazakhstan's silicon within a framework of Ka-

zPV project, which is a very good indicator. The left red side represents the bottom of the block, where high density of oxygen is concentrated from crucible during the process of directional solidification.

The right red zone represents the top of the block, where a high density of transition metals is concentrated that are segregated to the upper side of the ingot with respect to Scheil equation/law.

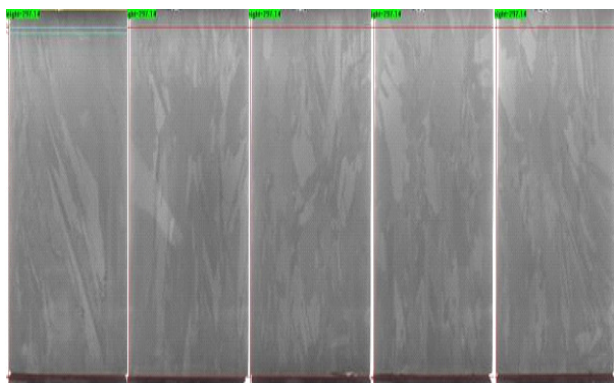


Fig. 3. Infrared imaging of blocks from ingot. The structure of the crystal grains is typical for polycrystalline solar grade silicon.

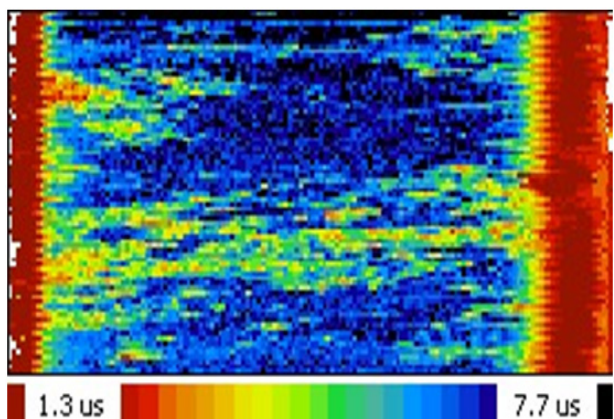


Fig. 4. Example of one block's lifetime mapping. Average lifetime measured for the ingot is 5.5 us. Such a lifetime value is typical for usual mc-Si ingots without compensation.

N-type of conductivity is absent in each block of the ingot thus more ingots height than generally can be used for solar cells production. Yield is about 81%.

Wafers produced after sawing of the blocks are also analyzed. The analysis implies to both physical (conductivity type, lifetime, resistivity, concentration of components and etc.) and to geometrical characteristics (thickness, shape, curvature, concavity and etc.) Table 2 describes specifications of wafers produced from Kazakhstan's silicon.

Table 2
Specifications of wafers

Item	Specification	Unit
Conductive Type; Dopant	P-Type, Boron	N/A
Resistivity	1-2.5 (99% per shipment)	Ohm-cm
Oxygen concentration	$\leq 5 \times 10^{17}$	Atoms/cm ³
Carbon concentration	$\leq 8 \times 10^{17}$	Atoms/cm ³
Lifetime	≥ 1 (99%) for wafer ≥ 6 for Ingot Average	us
Dimension	$156 \pm 0.5 \times 156 \pm 0.5$	μm
Nominal Wafer Thickness	200 ± 20	μm
TTV	≤ 30	μm
Bow	≤ 75	μm
Micro grain	Small grain area ≤ 2 cm ² ; 1 cm less than 10 grain	N/A

Figure 5 illustrates I-V characteristic of PV cell. Efficiency of the cell is 16.61% and corresponds to the efficiency of polycrystalline silicon cells manufactured by worldwide companies.

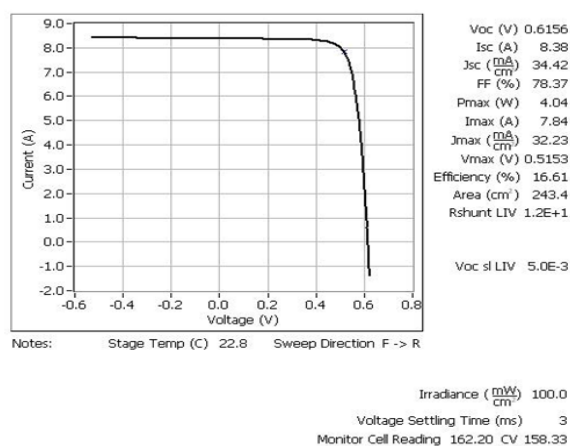


Fig. 5. I-V-curve of cell.

Conclusions

The refining technology of upgrading MGSi up to SoGSi has been worked out. The steps deal with selection of raw materials, carbothermic reduction of silica to produce MGSi and the first segregation of MGSi that takes place under the operation of Kazsilicon. The technologies for purification treatments, based on slag refining, acid leaching and seg-

regation should be transferred to the Kazsilicon in Ushstobe; for production of SoGSi, wafers and cells-Kazakhstan Solar Silicon in Ust-Kamenogorsk; and for production of solar panels with a total capacity of 60 MW – the Astana Solar Silicon in Astana.

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