ELECTRON BEAM SILICON PURIFICATION

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ABSTRACT: Vacuum rectification of highly doped N-type EG-silicon (As: 200 ppma) was conducted with use of electron beam as a heater. When background impurities' level for laboratory equipment was defined processes with varying power of electron beam were conducted in temperature range from melting point to the point of container destruction. Effective temperature of melt surface was calculated and it was revealed that temperature should be considerably higher than melting temperature, but it should enable container to be used for long period of time (not less than 1 hour) without container destruction. Increase of power and loads' mass further than 15 kgs led to contamination of silicon with metal impurities. We managed to avoid problems with container destruction and insertion of metal impurities while shifting to 50 kgs load thanks to improvements in technological process of purification and furnace design. Several CZ monocrystals (6", P-type, $\rho > 1$ Ohm*cm, $\tau > 10$ μs) were successfully grown from material obtained in 50 kgs load processes. According to our estimations, such purification effect was achieved at effective temperature of melt surface ca 2000K.
Keywords: Silicon, Cost reduction, Impurities, PV Materials, Recycling, Electron beam

1 INTRODUCTION

Purpose of the work was to study a possibility of using secondary electron grade silicon material (containing N-type dopants in concentrations as high as 200 ppma) as a feedstock for solar grade silicon manufacturing. In accordance with quality requirements for silicon the aim was set to purify initial heavily doped material to the level of concentrations less than 0.2 ppma.

Moreover, technological process has to be easily scalable and quantity of refined material during it should be enough for industrial use. Percentage of load of purified silicon to be used in manufacturing solar grade crystals should strive to 100%.

Previous works in the field do not cover problems arising when big amount of silicon is purified by electron beam. Neither key factors e.g. temperature and their evolution during load enlargement were revised enough by our predecessors. Thus our task was to study peculiarities of a laboratory refinement process and to transfer the technology to a large scale equipment.

2 METHODS AND FURNACE DESIGN

2.1 Furnace design

The furnace consists of chamber with cooled base plate in it. Graphite crucible with quartz crucible inside are placed on the base plate. Electron beam gun is mounted on the top of the furnace to provide heating. Scheme is provided at Figure 1.

In order to estimate impurities background of experimental furnace pure polysilicon (REC) of high quality was remelted. Parameters of original and resulting material are provided in Table I.

Table I: Impurities content

	Poly (REC)	After process	Solar grade spec
Donor, ppba	0.1	<3	<3000
Acceptor, ppba	0.03	-	<5000
Resistivity, Ohm*cm	500	80	>1

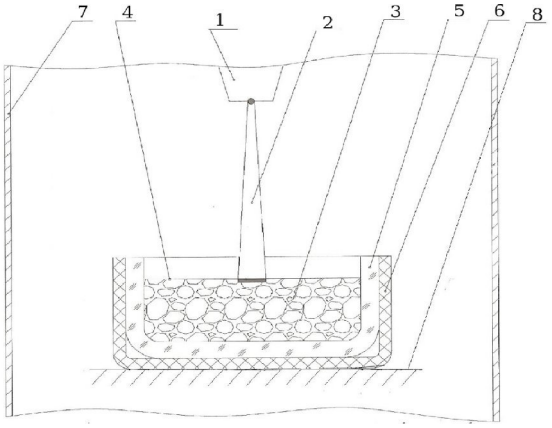

Figure 1: Furnace principal scheme: 1 — Electron beam emitter; 2 — electron beam; 3 — raw material; 4 — melt surface; 5 — quartz crucible; 6 — carbon crucible; 7 — chamber; 8 — cooled base plate.

2.2 Materials in question

Material containing excessive arsenic concentration was used for estimation of purification efficiency. The choice was made due to dopant's fugitiveness which on one hand enables refinement to be done in reasonable time compared to phosphorus, on the other hand dependence of purification process on several factors can be established what is impossible if antimony is concerned since rectification in this case is always swift.

2.3 Methods of quality control and temperature estimation

Quality of material obtained was tested by resistivity measurements and GDMS methods. Afterwards material was recrystallized by Czochralsky and directional solidification methods. Obtained crystalline samples were characterized by resistivity and lifetime range measurements.

Different modes of heating equipment operation were tested during experiments. Though employing maximal power during refinement leads to the best results in rates of material purification, instability of operation hampers such usage. Thus we tried to optimize working regime by estimating efficient temperature of melt surface using

following formula [1]:

$$\frac{\delta C}{\delta t} = -\frac{\beta A C_0 M_{Si}}{m\sqrt{2\pi RTM_{dop}}} e^{\frac{\Delta \overline{H} - \Delta G^0}{RT}},$$

where $\Delta\overline{H}$ — excessive heat of solution formation, ΔG^0 — free energy of dopant evaporation, M_{dop} — dopant's molar mass, T — temperature, A — area of melt surface, m — load mass, C_0 — initial dopant concentration, β — empirical parameter giving credit to geometry.

3 RESULTS AND DISCUSSION

3.1 Model process with small load

First purification processes were conducted with small loads ca 1kg. They provided information about possibility of material refinement. Also data collected enabled us to fulfill calculations and determine optimal efficient temperature of melt surface (See Table II). Effective temperature may be considered as a constant temperature of the whole mass of the load being in a state of equilibrium under which the same quantity of impurities would evaporate from the melt as it did in actual experiment.

Table II: Characteristics of small load processes

Load mass, g	Initial C_{dop}, ppma	Final C_{dop}, ppma	Final ρ, Ω*cm	T_{eff}, K	Time, min	Rate of refining, min^{-1}
1000	220	1-1.6	0.1-0.16	1707	60	2.82
1000	120	0.4	0.2-0.8	2187	15	20
1200	120	0.6	0.2	2533	10	20

3.2 Technology approbation with load mass of 15 kgs

We did not find any substantial (detectable with mass-spectral method) silicon contamination with materials of equipment when load (and heater power respectively) was increased to 15 kgs and process was conducted in 600mm chamber. Obtained material was tested for applicability for solar grade silicon production at PCMP. CZ monocrystals with diameter 150mm were grown (See Table III).

Table III: CZ ingots grown from material purified in 15 kgs loads

Ingot	Resistivity, Ohm*cm	Type	Lifetime, μs	Carbon level, ppma
1	5.1-16	100% N	26-45	1.66-5.4
2	2.0-4.3	100% N	31-40	1.18-4.6

3.3 Technology approbation with load mass of 25-35 kgs

Much bigger quantity of metallic impurities was detected in processed material with increase of load to 25-35 kgs. Tries of using such material as a feedstock for multicrystalline process have shown negative result. Resistivity of obtained material was homogeneous and in line with solar grade specifications, but lifetime was unsatisfactory. Resistivity measured by SWISS-wafers who manufactured the ingots is shown in Table IV. Lifetime was measured by Telecom-STV, results are presented at Figure 2.

Table IV: Resistivity in DSS sample crystallized from material obtained in purification process with load mass 25-35 kgs

Crystal	ρ, Ω*cm	Type	Geometry	Carbon level, ppma
1	1.8-2.3	100% P	225x225x140	3.5-5.2
2	3.5-4.0	100% P	225x225x140	2.6-4.1

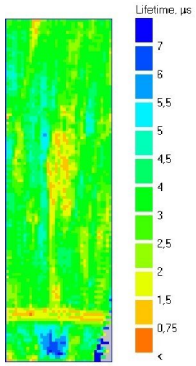

Figure 2: Lifetime distribution in DSS sample crystallized from material obtained in purification process with load mass 25-35 kgs

Furnace construction was modified leading to second generation equipment. It enabled us to decrease the content of metallic impurities (shown in Table V, concentrations given in ppmw) significantly and returned impurities levels to the minimum detectable with mass-spectral equipment.

Table V: Metallic impurities levels: Generation 1 furnace vs Generation 2

Generation	Fe	Ni	Cr	Mg	Al	Cu	Ti
1	30	0.3	0.5	0.4	0.2	0.03	0.2
2	0.2	0.02	0.06	0.04	0.06	0.01	0.06
Generation	Mn	Pb	Sn	Zn	Sb	Ca	
1	0.06	0.02	0.04	0.1	0.02	3	
2	0.02	0.02	0.02	0.07	0.02	0.5	

3.4 Technology approbation with load mass of 50 kgs

Further enlargement of load mass (process photo shown at Figure 3) did not led to the increase of metal impurities concentration, this fact enables us to hope that described process eventually can be successfully scaled up. Several 6" CZ monocrystals were successfully grown from resulting material at Prolog-Semicor, Kiev. At the beginning of the process the control sample has shown resistivity 3,5 Ohm*cm, afterwards the melt was doped in order to obtain P-type monocrystals (See Table VI).

Table VI: CZ ingots grown from material purified in 50 kgs loads

Ingot	Resistivity, Ohm*cm	Type	Lifetime, μs	Carbon level, ppma
1	1.6-1.8	100% P	> 10	< 2.9
2	1.3-1.55	100% P	> 9	< 3.0
3	1.6-1.8	100% P	> 12	< 1.6

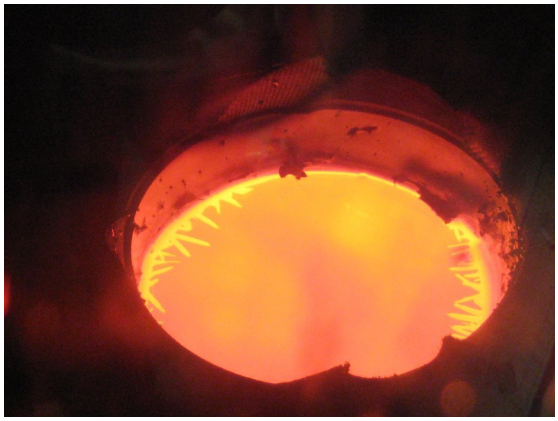

Figure 3: Photo of a process with 50 kgs load

4 CONCLUSIONS

We managed to avoid problems with container destruction and insertion of metal impurities while shifting upto 50 kg load thanks to improvements in technological process of purification. Several CZ monocrystals (6", P-type, $\rho > 1$ Ohm*cm, $\tau > 10$ μs) were successfully grown from material obtained. According to our estimations, such purification effect was achieved at effective temperature of melt surface ca 2000K. No refinement from carbon which is present in excess in some parts of secondary electron grade silicon occurs in developed process.

As a result we have developed technology for purification of heavily doped electron grade material from N-type impurities for different load masses varying from 15 to 50 kgs which can be scaled up to industrial volumes (150-300 kgs) yielding solar grade material.

Obtained CZ monocrystals suggest that our purified material is applicable for use as a feedstock for crystalline silicon production for solar energetics. Due to inability of purification from carbon preliminary material sorting is necessary before further refining. Percentage of use of the material in a load is determined by carbon concentration.

5 REFERENCES

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