PURIFICATION OF LEACHED METALLURGICAL GRADE SILICON BY ELECTRON BEAM MELTING

A. F. B. Braga(1), J. Otubo(1,2) and P. R. Mei(1)
(1) State University of Campinas, Dept. of Materials Engineering,
13083-970, Campinas, S P, Brazil, e-mail: jotubo@fem.unicamp.br
(2) IPEN/CNEN, Dept. of Materials Engineering, 05508-900, S. Paulo, SP, Brazil

Abstract

Silicon is commonly used to convert solar energy into electrical energy. To make this source of energy economically viable we should decrease the cost of silicon and solar cells devices. One of the possibility for the cost reduction is by the use of polycrystalline silicon. In this work we present the results of leached metallurgical grade silicon (MG-Si) purified by electron beam melting (EBM). The advantages of this process are to work in high vacuum (10^{-3}Pa) inside the chamber and the non existence of reaction between molten silicon and copper crucible. The parameters varied to prepare the samples were the electron beam power and beam incidence time on the molten pool. It was concluded that the process can reduce the impurity concentration of the Fe, Al, P, Cr, Ni, Cu and the C. The preliminary results look promising and the best result was 99.999% pure silicon.

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Introduction

The use of silicon to convert solar energy into electric energy is very common. However for the photovoltaic energy to compete in terms of cost with other sources of energy, the price, in module, of the solar cell device should be substantially reduced (1). That reduction can be made with the use of the polycrystalline silicon. In that sense several groups have been working with different processes to produce polycrystalline solar grade silicon (SG-Si) directly from the metallurgical grade silicon (MG-Si). One of the proposed processes to purify MG-Si is by electron beam melting (EBM). The advantages of this process are the high vacuum to eliminate impurity elements with vapor pressure higher than the one of the silicon and the elimination of the reaction between the melt and water cooled copper crucible.

The objective of this work is to study the purification of the MG-Si by EBM where the related literature is rare (2, 3, 4, 5, 6). Another motivation for this work is that the Brazil possesses one of the world largest quartz reserve, the raw materials for silicon production and it is also the one of the world largest producer of MG-Si (7). Besides that, the Brazilian MG-Si is one of the best in quality with 99.5 to 99.7% purity. Researchers from another countries have worked with 98-99% purity MG-Si (8, 9).

Experimental procedures

In this work it was used leached 150 to 250 µm MG-Si powder with 99.97wt% purity. The material was ultrasonically cleaned with acetone, rinsed in water and finally it was dried. The starting charge for each sample was 280g. The material was supplied by the RIMA Industrial SA.

The melting was done in an 80kW EB furnace, model EMO 80-LEW. The figure 1 shows the melting chamber and the water cooled copper crucible with the charge. Once charged, the chamber was closed and evacuated to initiate the heating. The heating was made by increasing the EB power in steps up to the point where all silicon had melted. On the molten material, the beam power was maintained for a certain time. After that time, the EB power was gradually decreased until its extinction. The varied parameters were the EB power and the time of beam maintenance on the liquid bath as can be seen in the Table I. The initial chamber internal pressure was the order of 10^{-3}Pa.

The carbon was determined by infrared spectroscopy (FTIR) in the 300µm thick samples, mechanically polished in diamond paste up to 0.25µm measured in the 605cm^{-1} wave number that characterizes the presence of the substitutional carbon. The same samples were used for resistivity measurement by the four points probe method using Keithley Instruments equipment, model 503. Al, Fe, P and B were analyzed by Glow Discharge Mass Spectrometry, VG Instruments, models VG 9000.

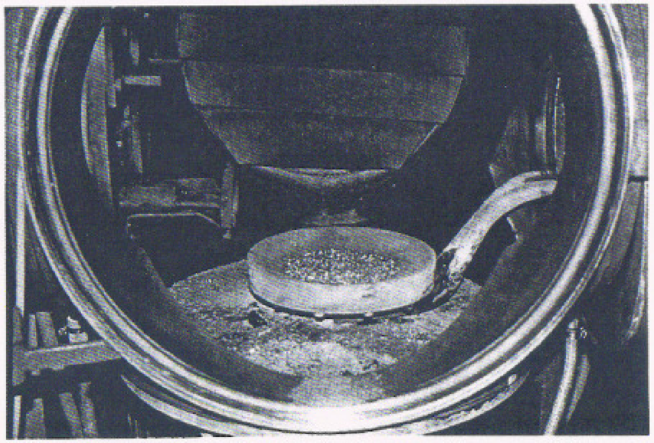

Figure 1. Melting chamber with charged water cooled copper crucible

Table I - Samples processing conditions

beam maintenance time (minute)	0; 10; 20
EB power (kW)	12; 16; 18,7
Initial chamber pressure (Pa)	10^{-3}

Results and discussions

In terms of processing, it was observed that minimum necessary EB power for melting 280g of silicon is 12kW. The upper limit for the same amount of material is 18.7kW for a 10 minutes of beam maintenance time. Longer time at this power promotes unstable process and the melt starts to stir. The process showed viable in the intermediate combinations of EB power and time. It was observed that the chamber internal pressure increases during the heating period due to degassing reaching values of the order of 10^{-1}Pa. Once the charge starts to melt, the chamber internal pressure remains high due to the evaporation of elements with vapor pressure higher than that of the silicon. For a longer time of EB incidence the chamber internal pressure start to decrease reaching 10^{-2}Pa. The best condition for the impurity removal was 16kW EB power with 20 minutes of beam maintenance whose sample is shown in the figure 2, top view. It was observed that the last part to solidify is the center of the sample because this is the most distant part in relation to the bottom of the water cooled copper crucible. Beside that, the EB power is decreased gradually and its extinction happens in the center of sample. A close look of figure 2 shows a series of loops on the sample surface indicating the solidification front. These loops, in fact, are isothermal loops indicating the existence of a temperature gradient toward the center like in a directional solidification. This fact was proved by chemical analysis. The top area, or center part, presents higher impurity content compared to the edge as can be seen in the Table II. For comparison it is also shown in Table II, the results obtained by Ikeda and Maeda (5). In the same manner, they used MG-Si purified by EBM using 50g samples. It can be seen that they did not succeed in removing boron, iron and the titanium. In our work it was seen that the removal of the boron is really difficult and the best result was a decrease of

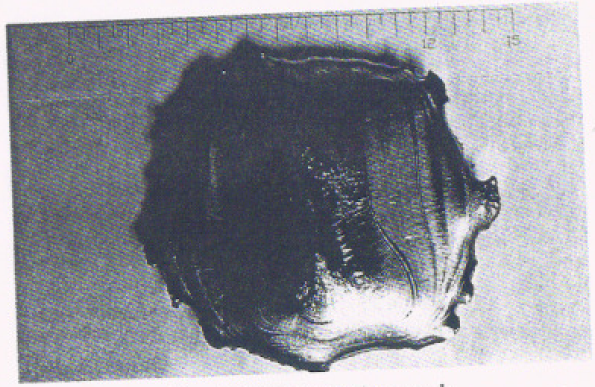

Figure 2. Top view of silicon sample

Table II Chemical composition of the sample before and after EBM (ppmwt).

Element	Ikeda (5)		(This work)		
	Raw material	After EBM	raw material	After EBM (edge)	after EBM (center)
B	15-20	15-20	13	7.9	11
Al	1800-2000	470	65	0.11	2.4
P	38-45	15	25	1	2.6
Ca	1300-1400	150	110	0.024	4.7
Ti	250-270	>270	2.8	0.001	0.31
V			0.2	<0.001	0.015
Cr			3.1	0.005	0.023
Mn			1.5	0.005	0.097
Fe	3200-3800	>3800	50	0.025	9.3
Ni			0.72	0.01	0.48
Cu			0.82	0.016	0.085
Zn			0.63	<0.1	<0.1
Sr			1	<0.05	0.079
Zr			0.37	<0.01	<0.1
C	150-180	15	540	0.5	
Remainder			23.83	0.624	0.851
Total metallic impurity (ppmwt in mass)	>7715	>4740	298	10	32
Removal efficiency (%)		39		97	89

in boron content near the sample edge. However, the removal of the iron and of the titanium was good and they were respectively of 99.95 and 99.96% with residual content of 0.001 and 0.025 ppmwt in mass. The removal efficiency of the other elements such as phosphorous, calcium and aluminum were respectively of 96.01, 99.8 and 99.98%, also determined near the sample edge. The carbon was reduced from 540ppmwt to 0.5ppmwt showing that the process is efficient to remove this element. In other processes like unidirectional solidification the carbon contamination is one of the problems because of the use of graphite crucible. Taking into account all the elements, the removal efficiency was 96.7% in the edge and of 89.2% in the top area. This tendency of the impurity concentration toward the center area of the sample could also be detected by electric resistivity measurement as can be seen in the Table III. For various processing combinations (beam power and beam maintenance time), the central part always presented smaller resistivity compared to the sample edge (~10 times smaller). Corroborating the data of chemical analysis, the best result with highest electrical resistivity was the combination of 16kW EB power and 20 minutes of beam maintenance on the melt. The result of 89% of impurity removal in the center part means that most of them are eliminated by evaporation process. Beside that, the removal of elements like boron and the titanium that have lower vapor pressure than the one of the silicon could indicate the compound formation with higher vapor pressure than that of the silicon.

Table III Electrical resistivity measurement

EB power (kW)	EB time maintenance (minute)	Sample region	Electrical Resistivity (Ω.cm)
16	10	center	0.03
16	10	edge	0.40
16	20	center	0.05
16	20	edge	0.60
18.7	10	center	0.08
18.7	10	edge	0.50

Starting with 99.97% pure MG-Si it was possible to obtain 99.999% pure silicon, near the edge of the sample, which could be considered solar grade silicon proving that the purification by EBM is a viable and promising process.

Conclusions

This work showed that the EBM is a viable process for MG-Si purification removing impurities such as: Fe, Al, Ti, Cr, Zr, Cu, Ni, P and C.

In terms of EB power and EB incidence time on molten silicon, it was concluded that the 12kW is the minimum necessary to melt 280g MG-Si and that the 18.7kW beam power with 10 minutes beam maintenance is the upper limit. Longer time or higher EB power make the process unstable. The 16kW EB power and 20 minutes beam maintenance on the molten silicon was the best condition for the impurities removal for 280g of starting charge.

Due to the temperature gradient, the center portion of the samples always presented higher impurity content. However, the efficiency of the removal in that part was 89% indicating that most of the impurities were eliminated by evaporation.

Starting with 99.97% pure MG-Si it was possible to purify to 99.999% pure silicon proving that the purification by EBM is viable and promising process.

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