The Purification of Metallurgical Grade Silicon by Electron Beam Melting: an Alternative to the Silane Processing Route

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Abstract

Brazil is one of the largest world producers of metallurgical grade silicon. Silicon is still the most widely used material for solar cells due to its high efficiency and also for its low cost. We present the results of leached metallurgical grade silicon (99.97% wt) purified by electron beam melting. The advantages of this method are: the high vacuum (10^{-3} Pa) inside the chamber (which eliminates certain types of impurities), and that there is no reaction between the molten silicon and the copper crucible. It also represents a possibility to eliminate the step of converting silicon into chlorinated compounds in the silicon purification processes, which would minimize minimizing the environmental pollution. Using 16kW electron beam (EB) power and 20 minutes of EB incidence on molten silicon, we obtained polycrystalline 99.999wt% pure silicon and we concluded that electron beam melting is a viable process for purifying metallurgical grade silicon.

Key words: metallurgical grade silicon purification, electron beam melting, solar grade silicon.

1. Introduction

Silicon is an element used in several technological applications such as: alloying elements (Fe-Si, Al-Si), production of solar cells, production of devices for the microelectronics industry, production of silicone and other products for the chemical industry, etc. For each application a different grade of silicon is used: metallurgical grade silicon (MG-Si), chemical grade silicon (QG-Si), solar grade silicon (SoG-Si) and electronic grade silicon (EG-Si). All of them start from the reduction reaction of silicon dioxide (SiO_2) in presence of carbon according to:

$$SiO_{2(s)} \quad + \quad 2C_{(s)} \longrightarrow Si_{(l)} \quad + \quad 2CO_{(g)} \qquad (1)$$

The impurities in the silicon are associated with that of the reduction process, that is, they depend on the quality of the raw material (SiO_2 and C). Compared to the available MG-Si in the world market, the Brazilian MG-Si presents higher quality.

Researchers from abroad [SAKAGUSHI, 1992; BATHEY, 1982] have presented in their works the use of MG-Si with 98 to 99wt% purity silicon while the Brazilian silicon has 99 to 99.5wt% purity.

The price of the MG-Si in the world market has varied in the last years between US$1.00/kg and US $2.00/kg. Today the cost is about US$2.00/kg. Figure 1 shows the world price variation of MG-Si in the last 10 years. Due to the large demand for this material, in 1996, the price of silicon reached its highest point of the last 10 years [TRUNZO, 1996]. Currently the supply and demand of silicon are nearly the same, however, the production capacity should be increased to assist the needs of the market for the future. The destination of demand is for two markets: 40% of the silicon is for chemical market (QG-Si) and 60% is for the metallurgical market (MG-Si) [FRAGOSO, 1988, TRUNZO, 1996].

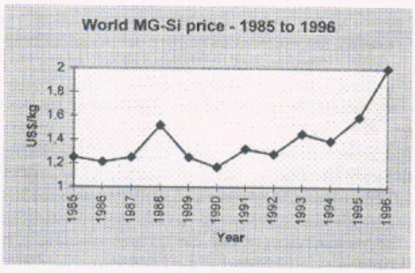

Figure 1 - World price variation of the MG-Si [TRUNZO, 1996]

The QG-Si is obtained according to the reaction shown in the equation 1 and corresponds to a material used in the silicone, electronics and ceramic industries. Compared to the MG-Si, the QG-Si should have a tighter chemical composition with maximum contents of 0.11wt% of aluminum, 0.28wt% of iron and 0.0026wt% of calcium. The total concentration of impurities should not be higher than 0.5wt% [SORHEIM, 1994].

The chemical industry segment has been growing. In 1980, Japan's consumption of QG-Si was 24% in relation to MG-Si and in 1993, this consumption reached 33%. Japan's projected consumption of QG-Si for the turn of the century is around 44% in relation to the MG-Si [MIYATA, 1994]. The growth expectation of the world consumption for the year 2005 for the QG-Si and for the MG-Si is indicated in the table 1 [TRUNZO, 1996].

Table 1 - World production of MG-Si and QG-Si:
current and projection for the year 2005 [TRUNZO, 1996].

Silicon	1996 (ton)	2005 (ton)	Growth (%)
QG-Si	351,700	676,400	92.3
MG-Si	481,000	626,200	30.2
Total (ton)	**832,700**	**1,302,600**	**56.4**

Among the several applications of silicon, the use of this material to convert solar energy into electrical energy is becoming a viable technology with low cost, using polycrystalline silicon as a solar cell. In agreement with what was said above, figure 2 shows the increase of the consumption of polycrystalline silicon to use as solar cells in the last 10 years. The driving force for this large increase of polycrystalline silicon consumption is the high cost of the single crystalline silicon [LAY, 1987]. The efficiency of energy conversion of polycrystalline silicon cells for industrial cells is of the order of 15% [SCHUBERT, 1996] while for research cells the efficiency is around 18% [PVPOWER, 1996].

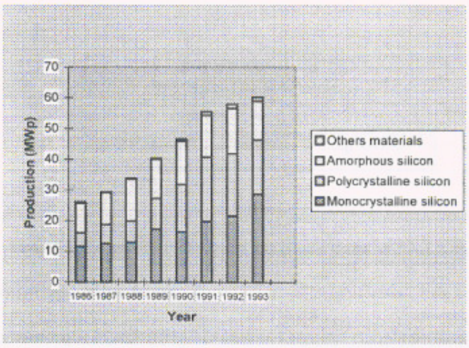

Figure 2 - World production of solar cells by types [NEDO, 1995].

Many research groups have been working to produce polycrystalline SoG-Si directly from the MG-Si. One of the proposed routes to purify MG-Si is the processing of the material in using an electron beam melting (EBM) furnace [IKEDA, 1993]. The advantages of this process are: the high vacuum (10^{-3}Pa) inside the chamber eliminates those elements with a vapor pressure higher than that of silicon, and the suppression of reactions between the water cooled copper crucible and molten silicon. In addition, the purification of MG-Si by EBM is an alternative to the silane (trichlorosilane) route, and thus reduces the environment contamination. The silane route is a several step route and in addition it needs one additional step, which is the unidirectional solidification to obtain SoG-Si. In comparison, the EBM is a one step process leading to a total cost reduction.

The two processes can be seen in figure 3.

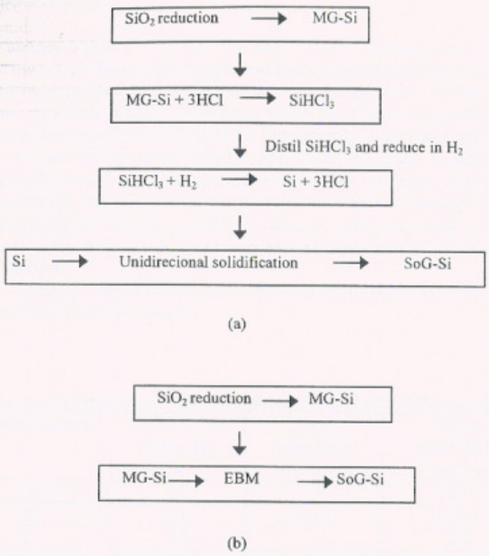

Figure 3. Comparison between (a) silane route and (b) EBM route

2. Experiment and Procedures

As a starting material, 280g of leached MG-Si, 100 to 250μm particle size powder was used. This material was washed with pure acetone and then it was dried. The purification of the material was carried out via an EBM furnace (model: EMO 80/LEW) operating at 16kW EB power with EB incidence on molten silicon for 20 minutes. The samples were melted in a water-cooled copper crucible with a bow shape.

The samples were characterized by a scanning electron microscope (SEM) (model: JEOL JXA 840). The samples were obtained by cutting slices around 5mm in diameter at different positions (edge and top center). To show the grain boundary, these sliced samples were polished and than treated with a solution of colloidal silica/KOH-20% (30 seconds for the samples taken from the top and 2 minutes for the samples taken from the edge). Chemical analysis was made by glow discharge mass spectrometry using an VG 9000 GDMS/VG Instruments spectrometer.

3. Results and discussions

The SEM images showed that Al, Ca and Fe are segregated at the grain boundaries and that the top portion of the sample had higher concentrations of impurities. This behavior could be explained by taking into account the geometry of the crucible, which is in the shape of a bow, and by the way in which the EB is extinguished. Upon melting, the last part of the sample to solidify is the top center because this position is the most distant part in relation to the water-cooled copper crucible surface. In addition, the EB power is gradually decreased and its extinction occurs in the top center of the sample, segregating the impurities in this position. It was also observed that the average grain size did not vary as a function of the melting conditions, rather it varied according to sampling position. The average grain size at top center was around 5mm and at the edge of the sample it was around 3mm.

As can be seeing in the Table 2, the chemical analysis confirmed that the impurities are segregating at the top center.

Table 2 - Chemical composition of the sample before and after EB melting.

Chemical element	Before EBM (ppm wt)	Edge After EBM (ppm wt)	Center After EBM (ppm wt)
B	13	7.9	11
Al	65	0.11	2.4
P	25	1	2.6
Ca	110	0.024	4.7
Ti	2.8	0.001	0.31
V	0.2	<0.001	0.015
Fe	50	0,025	9,3
Cu	0.82	0.016	0.085
Zr	0.37	<0.01	<0.1
Others	27.68	0.794	1.63
Total metallic impurities (ppm wt)	297.97	9.881	32.14
Final purity (wt%)	99.97	99.999	99.997

The EBM allowed purification of MG-Si from 99.97wt% to 99.997wt% at the top center and to 99.999wt% at the edge of the sample, demonstrating that the purification by EBM is a viable process.

4 . Conclusions

EBM is a viable method to purify MG-Si, removing impurities such as B, P, Fe, Al, Ca, Ti, V, and others.

With 16 kW EB power and maintaining the beam for 20 minutes, the sample purity obtained were 99.997wt% at the top center and 99.999wt% compared to 99.97wt% starting powder.

The geometry of the copper crucible and cutoff of EB power at the top center of the samples drive the segregation of impurities to this position.

The purification of MG-Si by EBM is an alternative method to the silane route to produce SoG-Si. It minimizes the environmental impact and could also reduce the total processing cost.

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