PURIFICATION OF POWDERED METALLURGICAL GRADE SILICON BY PLASMA TREATMENT

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ABSTRACT

A study was made of the purification of powdered metallurgical grade silicon with the objective of obtaining solar grade silicon. The approach used involved the successive acid leaching of the silicon using HCl and HF which resulted in a reduction of the impurity level from about 1.5% to less than 0.05%. While further leaching did not reduce the impurity level significantly, it was found that remelting the powder under plasma conditions followed by acid leaching reduced the impurity for most of the elements to the ppm level. The mechanism of the purification and an optimization of the treatment conditions is presently under study. While the product is still not of solar grade quantity, the plasma process seems promising.

INTRODUCTION

Over the last few years there has been a growing interest in alternative routes for the preparation of low cost high purity silicon that could be used in solar photovoltaic cells. A listing of some of the techniques presently investigated is given in Table 1. Of special interest are the sodium reduction of $SiCl_4$ in a plasma reactor developed by Fey and his co-workers at Whestinghouse (1) and the purification of metallurgical grade silicon by plasma zone refining developed by Amouroux and Morvan at the ENSCP (4).

The objective of the present investigation is to develop a new technique for the preparation of low-cost solar-grade silicon (SoG-Si) by the successive purification of powdered metallurgical-grade silicon (MG-Si). The incentive for such an approach is mainly economical since powdered MG-Si of a purity of about 98.5% is available in large quantities on a commercial basis for less the $1.0/lb. The task, however, is by no means an easy one since as shown in Table 2, the level of impurities present in the silicon has to be reduced by as much as four or five orders of magnitude. The approach used involved the following steps:

a. Purification of the MG-Si in powder form by successive acid leaching using HCl and HF solutions.
b. Melting of the powder in an induction plasma followed by the rapid quinching of the formed silicon droplets. This step can be followed by further acid leaching if necessary.
c. Final purification of the silicon using standard crystal growing techniques.

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EXPERIMENTAL TECHNIQUES

1. Acid leaching

The acid leaching was carried out on 50 g samples of the powdered MG-Si. These were mixed with a known volume of concentrated HCl and heated to boiling and maintained at that temperature for about one hour.

After filtering and washing, the silicon powder was mixed with dilute HF solution at room temperature for 10-12 hours. The powder was filtered, washed and dried.

2. Plasma treatment

Following the acid leaching, the powder was molten by passing it throught the discharge zone of an inductively coupled plasma. A schematic of the experimental setup used is shown in Figure 1.

The equipment comprised of a 50 mm i.d. air-cooled induction plasma torch of standard design operated at atmospheric pressure. The torch had a 3 turn induction coil connected to a 3 MHz, 25 kW r.f. power supply. The torch was operated with an Ar/H_2 mixture as the plasma gas. The sheath and the powder carrier gas were of pure argon. Under typical operating conditions the total gas flow rate through the torch was 55 ℓ/min and the tank circuit power was 15.4 kW.

The powder was introduced in the plasma at the center of the induction coil by gravity feeding from a fluidized bed feeder at a rate of 12 g/min. As the particles came out of the plasma zone, the silicon droplets were quenched and collected at the bottom of the water-cooled reactor.

3. Analytical techniques

In order to follow the progress of the purification process and the changes taking place in the particles the following analytical techniques had to be used at different stages of the investigation.

- Atomic absorption spectrophotometry.
  This served to follow the concentration of the impurities in the leaching solution and thus determine the effeciency of the leaching operation.
- Neutron activation analysis.
  This was used to determine the level of the different impurities in the silicon powder. The analysis was made using the slowpoke reactor at the university of Montreal.
- Optical and scanning electron microscopy.
  This provides means of examination of the surface caracteristics of the silicon particles during the different stages of the leaching and plasma treatment processes.
- X-ray fluorescence probe analysis.
  This analytical technique was used in an attempt to measure details of the concentration profiles of the impurities in the silicon granules after the plasma treatment. The results, however, were not conclusive since the concentration to be measured was lower than the detection limit of the instrument.

RESULTS AND DISCUSSION

The investigation was carried out using commercial powdered MG-Si supplied by Union Carbide Canada at Beauharnois, Quebec. Since the powder, as received, had a wide particle size distribution with more then 33% W smaller than 44 μm, it had to be classified before the purification process. This was particularly important in order to separate as much as possible of the fines (d_p < 10-20 μm) which would simply be vaporized in any subsequent plasma treatment operation. The particle size distribution of the powder used is given in Figure 2. It had a mean of 72 μm and a standard deviation of 25 μm. Figure 2 also shows the particle size distribution of the purified silicon. It is noted that the leaching and the plasma treatment results in relatively little change in the size distribution of the powder.

The results of Neutron activation analysis of a few key elements which were followed during the purification process are given in Figure 3. Superposed are the detection limits of the analysis technique and the purity objective required of the SoG-Si for a 10% photovoltaic cell effeciency.

It is noticed that the concentration of the different impurities decreases by almost one or two orders of magnitude as a result of the first leaching. Repeating this leaching did not seem to reduce the impurity level much further. The situation, however, changes after the plasma treatment where a further decrease of the impurity level was obtained during the second leaching. The effect is particularly evident for Ti, V, Mn and Cr.

In an attempt to explain the observed enhancement of the purification after the plasma treatment, a few scanning electron micrographs were taken of the silicon granules after the plasma treatment (Figure 4, magnification x 1000-5000). A close observation of the granules reveals a rather curious "tail" protruding from every particle. Detailed examination of the surface texture around these protrusions lead us to believe that these protrusions are the result of the rapid quinching of the molten silicon droplets at the exit of the reactor. Also apparent is the formation of fine crystals at the surface of the particles which, if containing a higher concentration of the impurities, could account for the relatively higher effeciency of the acid leaching operation following the plasma treatment.

CONCLUSIONS

The combination of the acid leaching and plasma treatment can be effectively used for purification of MG-Si. While the product so far obtained is not of solar-grade quality, it meets, for most of the elements, the purity requirement of the Czochralski's method for single crystal growing of solar-grade silicon.

ACKNOWLEDGMENT

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Table 1:-Summary of the different techniques presently under study by different laboratories for the preparation of solar-grade silicon

Company or Institution	Principal investigator	Approach used	Reference
Whestinghous, U.S.A.	M. Fey T. Mayer	$SiCl_4 + Na \rightarrow Si + NaCl$ plasma reactor, 3.5 MW	(1)
Union Carbide, U.S.A.	W.C. Breneman E.G. Farrier H. Morihara	$SiCl_4 + 2H_2 + Si \rightarrow 4HSiCl_3$ $4HSiCl_3 \rightarrow SiH_4 + 3SiCl_3$ $SiH_4 \rightarrow Si + 2H_2$	(2)
Dow Corning, U.S.A.	V.D. Dosaj L.P. Hunt A. Schei	$SiO_2 + C \rightarrow Si + CO$	(3)
ENSCP, Paris, France	J. Amouroux	purification of MG-Si bars by plasma zone refining	(4)
Université de Sherbrooke, Canada	M. Boulos	purification of powdered MG-Si by successive acid leaching and plasma treatment	

Table 2:-Typical analysis of the MG-Si and SoG-Si

Element	CONCENTRATION PPM BY WEIGHT		
	MG-Si (1)	Cz-Si (2)	SoG-Si (3)
Ti	308	5	0.002
V	22	5	0.004
Mn	302	5	0.039
Cr	35	5	0.037
Fe	10 400	25	0.040
Cu	54	5	0.045
Zr	-	-	0.065
Ni	-	-	0.420
Al	-	-	1.93
C	-	-	0.86

(1) Analysis of the MG-Si used in our investigation.
(2) Maximum impurity level for solar grade single crystal growing by Czochatlski's method.
(3) Upper limit of impurity for a 10% photovoltaic cell effeciency.

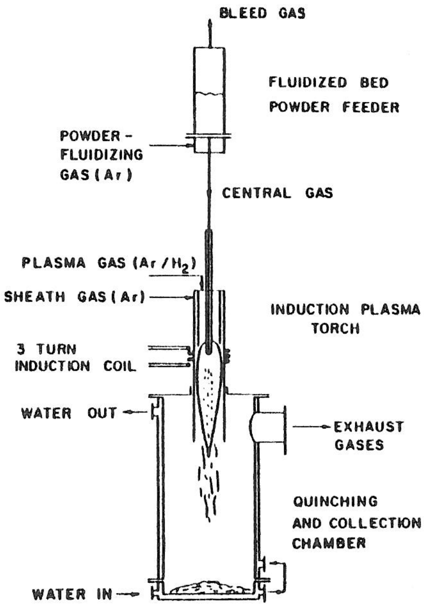

Figure 1:-Schematic of the experimental setup used for the plasma treatment.

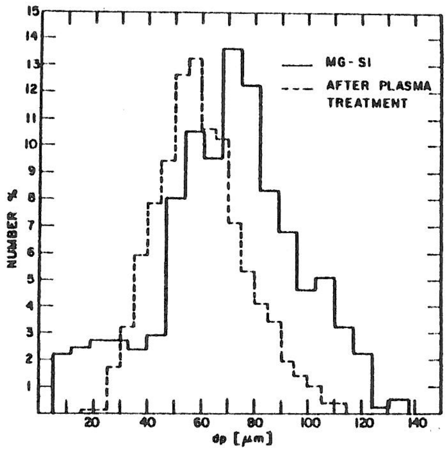

Figure 2:-Particle size distribution of the MG-Si and the silicon powder obtained after the plasma treatment.

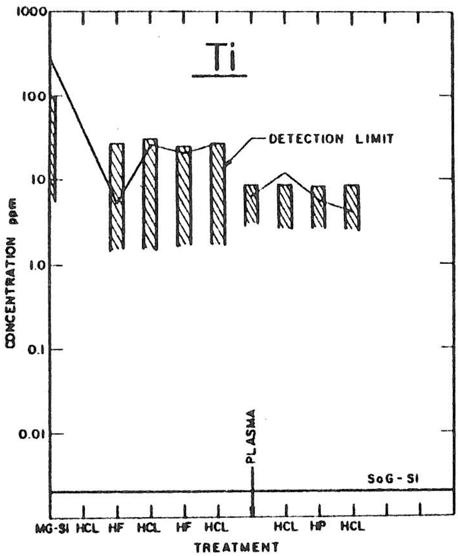

Figure 3-a:-Titanium concentration at different stages of the purification process.

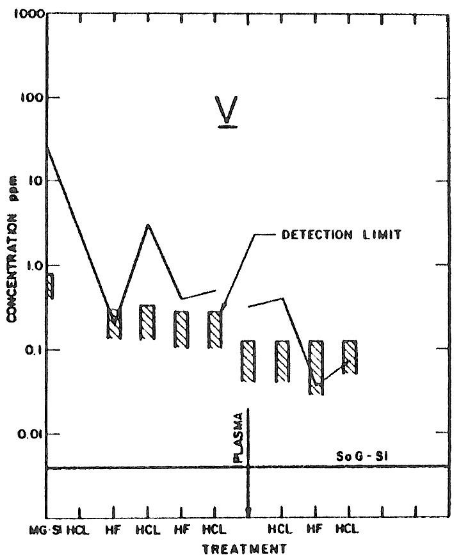

Figure 3-b:-Vanadium concentration at different stages of the purification process.

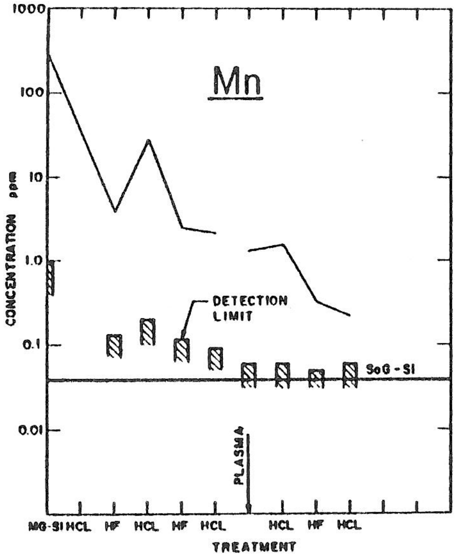

Figure 3-c:-Manganese concentration at different stages of the purification process.

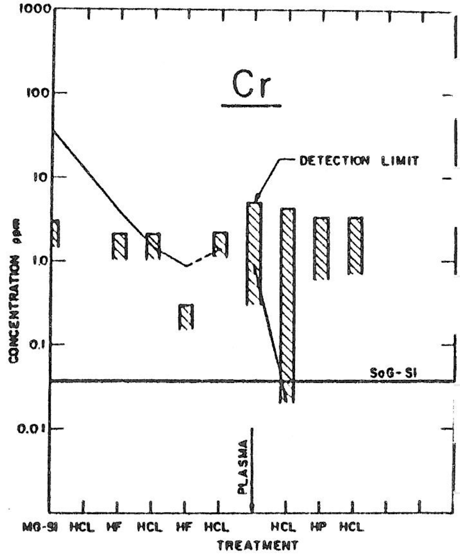

Figure 3-d:-Chromium concentration at different stages of the purification process.

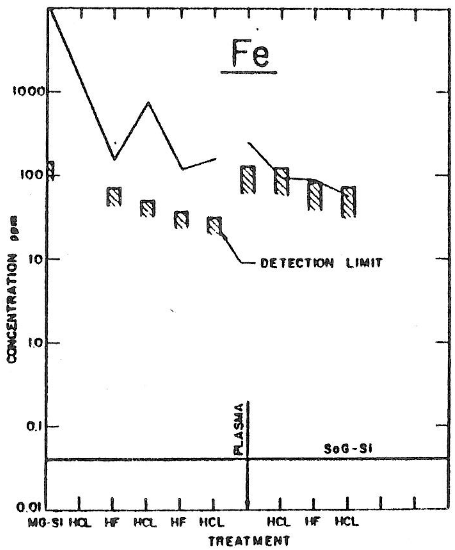

Figure 3-e:-Iron concentration at different stages of the purification process.

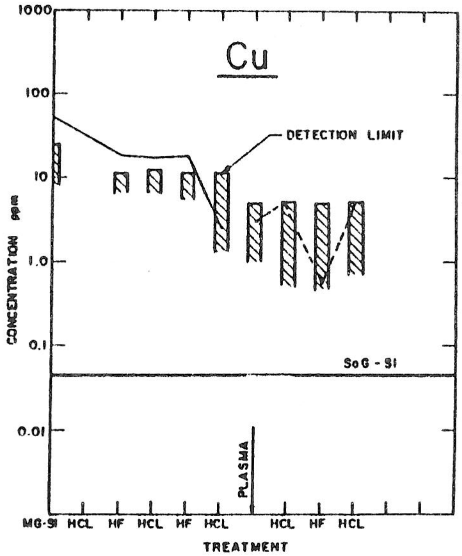

Figure 3-f:-Copper concentration at different stages of the purification process.

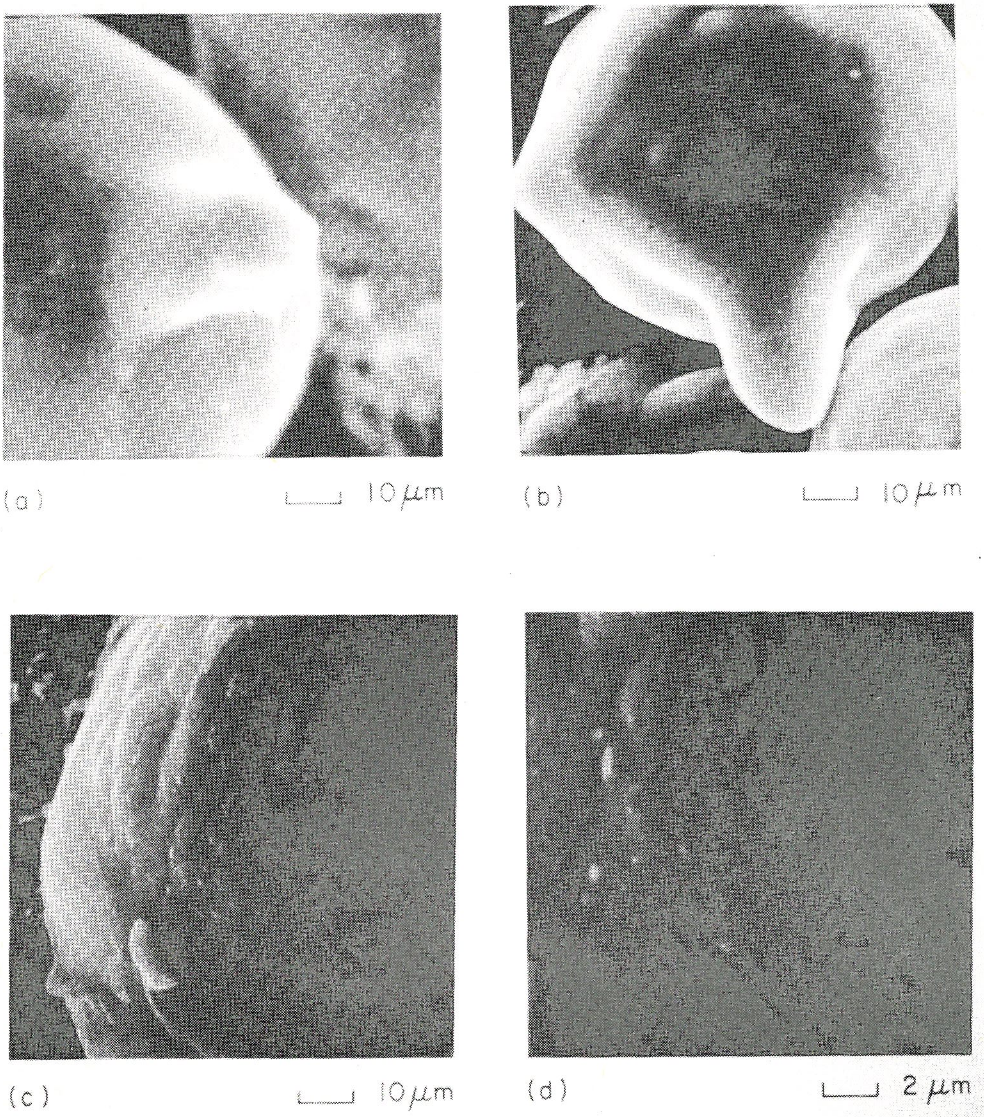

Figure 4:-Scanning electron micrographs of the silicon powder after the plasma treatment; Magnification (a)x1000, (b)x1000, (c)x1500 and (d)x5000