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Subcontractor Report

Production of Solar Grade (SoG) Silicon by Refining Liquid Metallurgical Grade (MG) Silicon

Final Report
April 19, 2001

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Crystal Systems, Inc.
Salem, Massachusetts

National Renewable Energy Laboratory

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ABSTRACT

The photovoltaic (PV) industry is undergoing rapid growth with the production of modules having approached 300 MW in 2000. At the projected 25% annual growth rate worldwide production will approach 18 GW by 2020 thus necessitating a large supply of silicon feedstock. Most commercial PV power generation is produced by crystalline silicon solar cells. A large supply of low-cost solar-grade (SoG) silicon feedstock specifically tailored for the PV industry must be developed to maintain this growth. The most direct approach is to upgrade metallurgical-grade (MG) silicon, but cost-effective reduction of boron (B) and phosphorus (P) has not been possible so far. This report summarizes the results of a 1998 awarded PVMaT subcontract to develop technology for producing SoG silicon by upgrading MG silicon with a cost goal of $20/kg in large scale production.

A Heat Exchanger Method (HEM) furnace originally designed to produce multicrystalline ingots was modified to refine molten MG silicon feedstock prior to directional solidification. Based on theoretical calculations, simple processing techniques, such as gas blowing through the melt, reaction with moisture and slagging have been used to remove B from molten MG silicon. The charge size was scaled up from 1 kg to 300 kg in incremental steps and effective refining was achieved. After the refining parameters were established, improvements to increase the impurity reduction rates were emphasized. With this approach, 50 kg of commercially available as-received MG silicon was processed for a refining time of about 13 hours. A half life of <2 hours was achieved, and the B concentration was reduced to 0.3 ppma and P concentration to 10 ppma from the original values of 20 to 60 ppma, and all other impurities to <0.1 ppma. Achieving <1 ppma B by this simple refining technique is a breakthrough towards the goal of achieving low-cost SoG silicon for PV applications.

While the P reduction process was being optimized, the successful B reduction process was applied to a category of electronics industry silicon scrap previously unacceptable for PV feedstock use because of its high B content (50-400 ppma). This material after refining showed that its B content was reduced by several orders of magnitude, to ~1 ppma (0.4 ohm-cm, or about $5x10^{16}$ cm^{-3}). NREL's Silicon Materials Research team grew and wafered small <100> dislocation-free Czochralski (Cz) crystals from the new feedstock material for diagnostic tests of electrical properties, C and O impurity levels, and PV performance relative to similar crystals grown from EG feedstock and commercial Cz wafers. The PV conversion efficiency of 1-cm^2 devices made from Cz crystals grown using the new feedstock were 95% as high as those from Cz crystals grown using EG feedstock and were comparable to those we obtained using commercial <111> Cz wafers. Devices with an efficiency of 7.3% were also made directly on wafers cut from the feedstock that had not gone through a controlled directional solidification. Only a few cells have been processed. Device parameters for this material have not yet been optimized, and additional diagnostic device fabrication, analysis, and verification is under way.

The successful B treatment process developed during the program can be utilized with high-B-doped silicon scrap from the electronics industry thereby making available, for the short term, a new silicon feedstock for an additional 200 MW/year annual production of PV modules. For the future, this approach when used in an MG silicon production plant will produce SoG silicon for $7.62/kg, which is less than the goal of $20/kg.

Production of Solar Grade (SoG) Silicon by Refining Liquid Metallurgical Grade (MG) Silicon

1. INTRODUCTION

The photovoltaic industry is undergoing rapid growth. Manufacture, sale and use of photovoltaics is a billion dollar industry with the production of modules approaching 300 MW in 2000. During the last four years, the annual worldwide production of photovoltaic modules has grown at an annual rate of 30 to 40 percent. This growth rate has varied in Japan showing from 40 to 60 percent. As the industry maintains it compound growth rate of 25%, the United States production will exceed 6 GW and worldwide production will approach 18 GW annually by 2020.

Most commercial PV power generation is produced by crystalline silicon solar cells. Their growth rate has been hampered by the lack of availability of low-cost solar grade (SoG) silicon feedstock. Currently, the excess capacity, rejects, and scraps from the semiconductor industry are being used as feedstock. The PV industry has to develop a lower cost SoG silicon feedstock that is not in competition with the semiconductor industry. Several attempts to produce SoG silicon feedstock have not resulted in a commercially viable product. The most attractive approach is upgrading metallurgical grade (MG) silicon, but this involves reduction of several impurities from high levels so that each impurity is reduced to < 1 ppma. Most of the impurities in MG silicon can be reduced effectively by directional solidification due to their low segregation coefficient. Boron (B) and phosphorus (P) are exceptions with segregation coefficients of 0.8 and 0.35, respectively. The simplest approach for upgrading MG silicon is to remove B and P chemically in the molten state followed by directional solidification.

During the late 1970's the Department of Energy (DOE) funded several options to produce SoG silicon for the photovoltaic industry, but the options that were ultimately developed produced semiconductor silicon. In addition to programs funded by the DOE, solar programs were also pursued in other countries and in the industry. However, none of these options resulted in commercial production of SoG silicon.

Recently, the National Center for Photovoltaics (NCPV) under DOE recognized the need to develop a low-cost silicon feedstock especially tailored to meet the requirements of silicon solar cell production. Therefore, a developmental effort was supported at CSI to optimize and scale up the refining procedures that were demonstrated in a previous research in development program to upgrade MG silicon to SoG silicon[1-3].

Previous approaches to upgrading MG silicon from the arc furnace or to purify silicon in the solid state using metallurgical techniques were not commercialized. The approach of the present program was to analyze and optimize the thermal chemical reactions that were proven in laboratory scale experiments and to scale up the process steps and demonstrate feasibility of the approach to produce low-cost SoG silicon by upgrading commercially available MG silicon.

This report documents the experimental effort carried out to refine commercially available as-received MG silicon using a modified HEM furnace by using combinations of techniques such as reaction with moisture, gas blowing, slagging, etc. for refining impurities, especially B and P, followed by a directional solidification. Initial results were obtained by refining 1 kg charge, and the charge was scaled up to 150 kg for refining. It was demonstrated that hot loading of the charge can be accomplished so that a 300 kg charge can be contained in the same crucible. By choosing the geometry of the crucible the same HEM furnace could be utilized to refine charges up to 500 kg. The goal of the program was to reduce all impurities to <1 ppma level including B and P. With commercially available MG silicon the B concentration was reduced to 0.1 ppmw (0.3 ppma) and the P concentration to 7 ppmw (6.3 ppma) and all other impurities to the 0.1 ppma level. After it was demonstrated that B can be effectively reduced, this procedure was tried on low-cost silicon scrap available from the semiconductor industry, which contains approximately 4 to 10 times as much B as MG silicon, but is otherwise essentially free of other impurities. This silicon scrap is available in abundance and can be used as another source of feedstock for the photovoltaic community in the short term. The B reduction process developed was used on this feedstock, and the B concentration was reduced from the 50-400 ppma range to <1 ppma. The refined material was used as feedstock for the Float Zone (Fz) and Czochralski (Cz) crystal growth. The Fz crystal was twinned and turned multicrystalline, whereas the Cz crystal was single and dislocation free. Test solar cells of 1 cm x 1 cm size fabricated at NREL demonstrated 7.3%, 12.5% and 13.4% efficiency for as-received, Fz and Cz grown crystals, using this refined material.

2. BACKGROUND

It has been postulated that SoG feedstock silicon can be developed using either a chemical or a pyro-metallurgical approach. In both cases, the starting point was metallurgical grade (MG) silicon and the target was to produce a high purity silicon feedstock for production of high performance devices.

The semiconductor industry used the chemical approach as it recognized that to achieve purities in the ppba range, MG silicon had to be converted into a gaseous or liquid chemical (e.g. trichlorosilane, silane, etc.), which is then put through multiple distillations for purification and finally reduced via gaseous phase reactions. The resultant product is high purity polysilicon, which is left with B and P at levels less than 1 ppba and all other impurities even lower. The residual elements, B and P, are the most difficult elements to remove from silicon.

With the metallurgical approach for purification of silicon, it is possible to achieve sub-ppma levels of impurities, but it is not feasible to achieve low ppba levels for semiconductor application. Refining of MG silicon involves upgrading reactions in the molten phase of silicon where diffusion and reaction rates can be higher compared to the solid state. Molten silicon with low B, P and SiC concentration must be directionally solidified to remove other metal impurities. If the refining approach works to upgrade MG silicon to levels where it can be used for the photovoltaic industry, it would represent a virtually inexhaustible supply of SoG silicon. In addition, it is recognized that the cost of production of SoG silicon using the refining approach can meet the requirements of the photovoltaic (PV) industry.

Solar cells are devices that are far more tolerant of impurities than the devices produced in the semiconductor industry. At the present time, the PV industry relies on silicon scraps from the semiconductor industry as feedstock. Almost all commercially produced solar cells utilize B-doped (p-type) silicon wafers in the 1 ppma range, and these devices rely on a p-n junction which is produced by incorporating a thin P-doped (n-type) layer on the p-type wafers. While there are differences in requirements for different solar cell processes, almost all commercial operations require the wafers to be >0.5 ohm-cm, p-type (0.2 ppma B) resistivity. Typical B concentration in MG silicon is 20-60 ppma. This means that the photovoltaic industry reduces this B concentration to < 1 ppba level and then puts back 0.2 ppma B during the production of wafers. Several studies[4,5] have documented the effect of impurities on the degradation of silicon solar cell performance. It is concluded that almost all impurities have to be less than 1 ppma, and, in some cases, at the ppba level. Fortunately, elements that degrade performance in the ppba range have segregation coefficients in the 10^{-8} range and can therefore be removed to this level by controlled directional solidification.

The cooperative effort between Exxon and Elkem demonstrated[6] that it is possible to upgrade MG silicon in the arc furnace and use it as feedstock for photovoltaic applications. Several approaches to upgrade MG silicon[7] in an arc furnace were pursued in Germany, but these efforts were curtailed without commercialization. Similarly, other approaches[8-20] did not result in a product.

Programs to upgrade MG silicon have also been supported in Japan. Work in Japan has shown[21] that it is possible to upgrade MG silicon for photovoltaic applications, and Kawasaki Steel Corporation set up a pilot production facility to demonstrate the full process under funding from NEDO. In this process, high purity MG silicon P concentration is reduced under vacuum, followed by reduction in Al and Fe levels by a first directional solidification step. Boron is then removed from the surface by reaction with Ar plasma and water vapor, and finally a second directional solidification produces SoG silicon. Laboratory results are encouraging with respect to reducing impurities, but vacuum processing, two directional solidifications and treatments in Ar plasma make it difficult to produce SoG cost effectively.

The approach in this program is different from the Elkem and Kawasaki approaches. However, it addresses the essential components of both these approaches and is based on laboratory results[1,2] which have shown that each of the impurities in MG silicon can be reduced to less than 1 ppm level (including B and P) by carrying out purification of molten silicon. The initial purification approaches were developed by Crystal Systems using commercially available MG silicon as feedstock and the Heat Exchanger Method (HEM™) for purification. These laboratory experiments were carried out with a ~3 kg charge and involved stirring the melt by blowing it with moist argon, slagging and volatilization in the molten state of silicon followed by directional solidification. Based on encouraging laboratory results, experiments were carried out in an MG silicon production plant where molten MG silicon from a standard production furnace was poured into a ladle and laboratory-developed procedures were used prior to solidification of the silicon. These experiments were carried out on a tap charge of approximately 1200 kg, and the purification experiments were limited to less than one hour duration prior to solidification of the charge. It was demonstrated that significant purification of the charge was achieved. However, it was recognized that the purification approaches have to be utilized for longer periods of time to produce SoG silicon.

3. OUTLINE OF CURRENT PROGRAM

The Department of Energy (DOE) in cooperation with the U.S. Photovoltaic Industry initiated the Photovoltaic Manufacturing Technology (PVMaT Project) in FY1991 to work on key problems of the industry. It has been recognized that availability of solar grade (SoG) silicon is necessary for the future growth of the photovoltaic industry. In view of this, the PVMaT awarded a cost sharing subcontract with Crystal Systems, Inc. (CSI) to refine MG silicon in the liquid state with the HEM and using thermochemical reactions to produce low-cost SoG silicon feedstock for the photovoltaic industry. The work involved process development on a laboratory scale for refining commercially available MG silicon to produce SoG silicon. Emphasis was on prototype equipment and procedures development, optimization and verification of the purification process for eventual use in a foundry or MG silicon production plant. After process development, focus would shift to scaling up to 450 kg charge size. The development and implementation of this upgraded SoG silicon feedstock production process is expected to result in significant cost saving and increased throughput with a projected production cost of SoG to be less than $20/kg.

Some of the topics of focus during the program involved:

- Evaluating commercially available MG silicon from various suppliers,
- Analyzing on theoretical basis, refining processes for MG silicon in the molten state,
- Developing equipment and procedures for upgrading MG silicon to SoG grade level for charge sizes up to 50 kg MG silicon,
- Scaling up charge sizes and evaluating efficiency of refining,
- Evaluating crucible materials for refining,
- Determining the thermo chemical reactions for reduction for B and P,
- Developing procedures for B reduction in MG silicon during refining,
- Developing procedures for P reduction during refining,
- Evaluating reduction of metallic impurities during refining and directional solidification,
- Developing a model for B reduction,
- Optimizing parameters for improving rates of impurity reduction during refining,
- Developing hot loading of feedstock so shorter crucibles can be used for refining,
- Evaluating refining of 450 kg charge sizes,
- Carrying out refining experiments,
- Performing characterization of material and analysis consistent with theoretical and experimental results,
- Developing plans for production of SoG silicon in large scale manufacture, and
- Estimating costs of production of SoG silicon in production.

Within this scope, the project was initially focused on developing refining procedures, setting up experiments consistent with the theoretical analysis and evaluating experimental data. Thereafter, emphasis was placed on optimizing procedures for B and P reduction during refining and scaling up the charge size to 50 kg and achieving B and P and other impurities to less than 10 ppma each. Based on successful completion of these Phase I goals, emphasis of Phase II was to show technical feasibility of producing SoG silicon. This was to be accomplished by scaling up the charge sizes to 450 kg, reducing all problematic impurities to <1 ppma levels and using the SoG in prototype production for the large scale manufacture of silicon wafers for solar cell applications.

4. MG SILICON FEEDSTOCK

Several MG silicon suppliers worldwide were contacted to supply samples of their commercially available product for evaluation and testing in the present program. The program goals were outlined to the MG silicon suppliers, and it was stressed that the most problematic elements were B and P. If possible, commercially available MG silicon with low B and P was desirable. Except in a few instances, most suppliers do not analyze MG silicon for B and P. The general trend is to characterize MG silicon for Fe, Al, Ca and Ti by the producers. In most cases, the purity of silicon is rated between 99% and 99.7%.

Seven suppliers agreed to provide their commercially available MG samples. These samples were analyzed using glow discharge mass spectroscopy, and the data is shown in Table I. It can be seen that there are many impurities detected, and the major impurities are Fe, Al, Ca and Ti. The impurity levels vary for different sources of MG silicon. The range of B and P for the seven samples characterized showed 5-50 and 25-50 ppmw, respectively. It is important to point out that MG silicon is quite inhomogeneous when analyzed from the viewpoint of ppm levels of impurities. Therefore, the analyses shown in Table I should be viewed as typical levels within a wide range rather than as absolute values. The present program was to refine MG silicon in the molten state followed by a directional solidification step to remove impurities that have a low segregation coefficient. The most important elements that have to be removed during the refining step are B and P because of their high segregation coefficients.

During initial stage about 30 kg samples were procured and tested. Later, larger quantities of 500 kg and 1 ton batches were obtained from selected suppliers. Contact is being maintained with the suppliers to keep them in touch with the progress of the project so as to keep them interested. In addition, meetings have been held with several MG silicon producers and potential customers to discuss mutual interests. At the present time there have been exchanges of data and discussions of future prospects but no commitments have been made yet.

Some of the personnel involved in the program have visited or carried out experiments in MG silicon plants. Therefore, there is a familiarity with the operations and procedures carried out in MG silicon plants. Wherever possible, refining procedures are being developed in such a way that they can be adopted in MG silicon production plants.

In the present program commercially available, as received MG silicon from the supplier has been refined to reduce impurities. In large scale production it is anticipated the molten MG silicon will be tapped from an arc furnace directly into a ladle with a heat source where the refining can be carried out and thereafter the charge directionally solidified.

Table I. Analysis of Metallurgical Grade (MG) Silicon Samples from Various Suppliers (in ppma)							
Element	1	2	3	4	5	6	7
Li	0.239	0.526	0.607	0.308	0.344	0.117	11.734
Be	-	-	-	-	-	-	0.312
B	52	70	21	15	18	130	78
Na	0.33	0.33	0.17	0.53	0.16	0.23	1.09
Mg	0.7	7.3	0.6	2.4	8.4	1.5	1.8
Al	234	781	14	109	130	546	677
Si	Major	Major	Major	Major	Major	Major	Major
P	27	32	45	27	23	41	27
S	0.11	0.10	0.14	0.14	0.10	0.50	1.49
Cl	0.67	0.43	0.45	0.47	0.48	0.69	4.12
K	0.86	0.08	0.29	0.32	0.23	0.11	4.17
Ca	2	214	6	123	53	1	63
Sc	0.07	0.31	-	-	-	0.14	0.40
Ti	26	94	3	18	16	132	6
V	1.378	5.347	0.143	0.336	17.640	27.562	0.276
Cr	1.674	8.100	0.211	1.026	3.348	3.510	2.484
Mn	12.271	69.025	6.136	10.737	23.008	6.136	0.920
Fe	365	1408	101	319	339	870	176
Co	0.810	3.574	0.041	0.119	0.362	1.096	0.071
Ni	1.627	7.657	0.220	0.373	10.528	11.006	0.316
Cu	5.304	12.376	0.442	1.503	1.768	4.420	1.503
Zn	0.095	0.159	0.043	0.034	0.020	3.480	0.095
Ge	1.470	3.095	0.464	0.851	0.542	1.006	1.277
As	0.232	0.180	0.037	0.225	0.184	0.139	0.139
Se	<0.178	<0.178	<0.178	<0.178	<0.178	<0.178	<0.178
Sr	0.132	1.452	0.068	0.000	0.316	1.000	0.774
Y	0.148	0.379	0.005	0.442	0.041	0.142	0.152
Zr	0.770	3.387	0.139	0.015	0.431	24.631	0.801
Nb	0.060	0.236	0.011	0.453	0.021	0.251	0.017
Mo	0.100	0.703	0.059	0.029	0.214	0.732	0.029
Ru	-	-	-	0.033	-	-	-
Ag	<0.130	<0.130	<0.130	<0.130	<0.130	<0.130	<0.130
Cd	<0.075	<0.075	<0.075	<0.075	<0.075	<0.075	<0.075
Sn	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	0.028
Sb	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	0.012
Ba	0.123	0.818	0.012	0.082	0.348	0.022	0.695
La	0.465	1.759	0.011	0.055	0.069	0.728	0.089
Ce	1.042	3.007	0.032	0.100	0.104	2.405	0.261
Pr	0.144	0.399	0.005	0.017	0.017	0.319	0.028
Nd	0.370	1.071	0.016	0.043	0.053	1.013	0.072
Sm	0.045	0.187	-	-	0.014	0.052	0.016
Eu	-	0.016	-	-	-	<0.006	<0.006
Gd	-	0.084	-	-	-	0.077	0.021
Tb	-	0.016	-	-	-	0.013	<0.006
Dy	-	0.078	-	-	-	0.055	0.016
Ho	-	0.015	-	-	-	0.009	<0.006
Er	-	0.039	-	-	-	0.012	0.012
Tm	-	0.004	-	-	-	<0.006	<0.006
Yb	-	0.042	-	-	-	0.008	0.006
Lu	-	-	-	-	-	<0.006	-
Hf	-	0.035	-	-	-	-	0.017
W	0.037	0.139	0.013	0.004	0.009	0.038	0.021
Pb	<0.007	<0.007	<0.007	<0.007	<0.007	0.009	<0.007
Bi	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Th	0.029	0.031	0.002	0.004	0.007	0.169	0.010
U	0.017	0.041	0.001	0.003	0.005	0.097	0.007

5. REFINING OF MG SILICON IN MOLTEN STATE

A review of the typical impurity analysis of MG silicon shows that most of the impurities can be removed by directional solidification as most impurities have a low segregation coefficient in silicon. The problematic elements are B and P, which cannot be removed effectively from silicon by directional solidification. Therefore, while directional solidification from the molten state has to be a key refining step, it is necessary to develop additional refining procedures focused on removing B and P from molten silicon prior to directional solidification. It is desirable that all impurities including B and P be reduced from MG silicon as much as possible prior to directional solidification to yield a high amount of SoG silicon. In view of these features, emphasis was placed on developing refining procedures and evaluating their effect on all impurities in MG silicon. This study used several simple refining procedures to upgrade molten MG silicon and follow the refining step with directional solidification.

Evacuation. The simplest refining step is to remove volatile elements from MG silicon; heating MG silicon in a molten stage under vacuum can enhance this. Table II shows the elements that can be removed under vacuum. A major advantage of this refining step is that the impurities (and their residual effects) are removed from the MG silicon. Vacuum processing of molten silicon has been shown to be effective for reducing P concentration in silicon, as well as Al, Na, Mg and volatile elements such as, S and Cl.

Formation of volatile species. If the impurity elements can be reacted to form volatile molecular species, further refining can be achieved. Table II also shows that the elements after reaction can be removed through the vapor phase by complexing with O, H and/or Cl. Volatile products of impurities can be formed by reaction with solid powders or gases. The solid powders could be added to the initial charge of MG silicon prior to melting or to the molten charge with the reactive gas.

Oxidation of impurities. Impurity elements in MG silicon can be oxidized to form other species and separated from MG silicon in a slag. In this case, the species formed has to be more stable than the element remaining in MG silicon. Therefore, thermodynamic analyses are necessary to predict if this is possible, and then experimental conditions have to be developed conducive to forming the impurity oxide species. Table II shows the oxidation potential and slag basicity required to remove impurities, and Table III shows some of the species that were studied for refining of impurities.

Development of a thermodynamic database and model to delineate kinetic from equilibrium effects was prepared using a database in HSC modified to include thermodynamic data and solution models. HSC is a commercially available thermodynamic modeling package that incorporates an extensive database, allows extensive modification of the database and solution models by the user, and includes several powerful Gibbs Free Energy minimization routines. Overview thermodynamic calculations were performed initially with this database in the system Si-B-P-H_2O-Ar, starting with 1 mole of Si(l) containing 30 and 40 ppm of B and P, respectively. The calculations were performed to simulate the addition of up to 20 moles of gas to the system.

Table II. Refining approaches for removing impurities from liquid MG silicon						
Atomic #	El.	Volatilization (Liquid to Vapor)		Slagging (Liquid to Liquid) (all require some oxidation potential)	Sequestering (Liquid to Solid)	Segregation (Liquid to Solid)
		Elemental	Complexed Vapor Species*			Log Seg. Coeff. (Lower is better)
3	**Li**	High	LiCl(g)	Moderate (acid)		
5	**B**	V. Low	HBO	Moderate (basic, oxidized)		-0.1
9	**F**	High	NaF	Good	Si_3N_4	
11	**Na**	High	NaCl	Moderate, (acid)		
12	**Mg**	High	$MGCl_2$	Moderate, (acid)		-5.5
13	**Al**	Moderate	AlCl, $AlCl_3$	Good		-1.5
14	**Si**		$SiCl_2$, SiO			
15	**P**	Moderate	P_2, also PH_2, (PH, PH_3) or PO	Good (basic, oxidized or extremely reduced)		-0.5
16	**S**	High	SiS, H_2S, HS, SiS_2, S_2	Good (basic, reduced or extremely oxidized)		
17	**Cl**	High	(NaCl)	Moderate (basic, reduced)		
19	**K**	High	KCl	Moderate (acid)		
20	**Ca**	High	$CaCl_2$	Good (acid)		
21	**Sc**	Low	$ScCl_2$			
22	**Ti**	V Low	$TiCl_2$, $TiCl_3$			-5.7
23	**V**	V. Low				-5.4
24	**Cr**	Low		Moderate (oxidized)		-4.9
25	**Mn**	high		Moderate (oxidized)		-4.9
26	**Fe**	V. Low	$FeCl_2$	Moderate (oxidized)		-5.2
27	**Co**	V. Low	$CoCl_2$	Moderate (oxidized)		-4.7
28	**Ni**	V. Low	$NiCl_2$	Moderate (oxidized)		-3.9
29	**Cu**	Moderate	CuCl	No		-3.1
30	**Zn**	V. High	($ZnCl_2$)	No		-5.0
31	**Ga**	High		Good		
32	**Ge**	Low		Good	SiO_2	
33	**As**	High				
34	**Se**	V. High				
37	**Rb**	V. High	RbCl	Moderate (acid, oxidized)		
38	**Sr**	V. High	$SrCl_2$	Good (acid, oxidized)		
39	**Y**	V. Low				
40	**Zr**	V. V. Low				-7.8
41	**Nb**	V. Low				-6.4
42	**Mo**	V. V. Low				-7.3
47	**Ag**	High		No		-4.8
48	**Cd**	High		No		
50	**Sn**	Moderate				-1.5
51	**Sb**	V. High				
56	**Ba**	V. High (?)	$BaCl_2$			
57	**La**	V. Low				
58	**Ce**	V. Low				
59	**Pr**	Low				
60	**Nd**	Low				
62	**Sm**	V. High (?)				
63	**Eu**	V. high (?)				
64	**Gd**	V. Low				-6.4
65	**Tb**	V. Low				
66	**Dy**	High (?)				
74	**W**	E. Low				-7.8
82	**Pb**	V. High				
83	**Bi**	V. High (?)				
90	**Th**	V. Low				

*Calculated for 1 bar pressure, injected gas consisting of 45% Ar, 45% HCl and 10% H_2O. Parenthesis indicates a lower abundance than the elemental species at the conditions considered. Question marks indicate calculated results of questionable reliability.

Table III. Species used in initial thermodynamic analysis of Ar + H_2O + H_2 addition to Si bath with B and P impurities. The highlighted species are stable

#	Phase	Species	#	Phase	Species	#	Phase	Species
1	gas	Ar(g)	22	gas	HBO_2(g)	43	gas	P_4O_9(g)
2	gas	H_2O(g)	23	gas	H_3BO_3(g)	44	gas	P_4O_{10}(g)
3	gas	B(g)	24	gas	$(HBO_2)_3$(g)	45	gas	Si(g)
4	gas	B_2(g)	25	gas	HPO(g)	46	gas	Si_2(g)
5	gas	BH(g)	26	gas	O_2(g)	47	gas	Si_3(g)
6	gas	BH_2(g)	27	gas	OH(g)	48	gas	SiH(g)
7	gas	BH_3(g)	28	gas	P(g)	49	gas	SiH_2(g)
8	gas	B_2H_6(g)	29	gas	P_2(g)	50	gas	SiH_3(g)
9	gas	B_5H_9(g)	30	gas	P_3(g)	51	gas	SiH_4(g)
10	gas	$B_{10}H_{14}$(g)	31	gas	P_4(g)	52	gas	Si_2H_6(g)
11	gas	BO(g)	32	gas	PH(g)	53	gas	SiO(g)
12	gas	BO_2(g)	33	gas	PH_2(g)	54	gas	SiO_2(g)
13	gas	B_2O(g)	34	gas	PH_3(g)	55	solid	B_2O_3
14	gas	B_2O_2(g)	35	gas	PO(g)	56	solid	H_3PO_4
15	gas	B_2O_3(g)	36	gas	PO_2(g)	57	solid	P_2O_5
16	gas	$B(OH)_2$(g)	37	gas	P_2O_3(g)	58	solid	SiO_2
17	gas	$B_2(OH)_4$(g)	38	gas	P_2O_4(g)	59	solid	BP
18	gas	$(BOH_)_3$(g)	39	gas	P_3O_6(g)	60	liquid	B(l)
19	gas	H(g)	40	gas	P_4O_6(g)	61	liquid	P(l)
20	gas	H2(g)	41	gas	P_4O_7(g)	62	liquid	Si(l)
21	gas	HBO(g)	42	gas	P_4O_8(g)	Fi		

This system was expanded to include Ca and Al as well, and slag calculations incorporated the B-P-Na-Ca-K-Al-Si-O system. Removal of impurities from liquid silicon requires (a) reaction, such as oxidation, to form an impurity species, and (b) partitioning of this species from liquid silicon into a second phase.

For example, B in Si (l) can react with H(g) and SiO(g) to form HBO(g); therefore, B reacts to form HBO and is removed by partitioning to the vapor phase and removed from liquid silicon, or

$$\underset{(g)}{SiO} + \underset{(g)}{\tfrac{1}{2}H_2} + \underset{(\ )}{B} \leftrightarrow \underset{(g)}{HBO} + \underset{(\ )}{Si}$$

In addition to the vapor, the impurity species can also partition into a liquid phase such as a slag, or into a solid phase such as Si_3N_4 or SiO_2. Alternatively, the impurity can be partitioned into a residual liquid as silicon is partitioned to the solid as in directional solidification.

A large number of species were considered[22]; the species used in the vapor phase removal calculations are listed in Table III. Preliminary analysis of the thermodynamics of the process indicates that the observed removal of B and P during steam blowing cannot be explained in terms of reduced B and P species volatilities. Under equilibrium conditions, less B and P are partitioned to the vapor phase than in liquid silicon, resulting in increasing concentrations of B and P in the residual silicon liquid. However, HBO is a stable species in the vapor phase over a wide range of conditions, and is considered to be the most important species for removal of B to the vapor.

Slagging. If an impurity can be reacted to form a non-volatile species, it may be possible to incorporate the species or a combination of species to form a second phase, thereby sequestering the impurity away from MG silicon into this "slag" phase. This slag phase can either float on the surface of molten silicon or sink to the bottom of the crucible and be easily removed. A synthetic slag can be added to the charge for refining or formed as a result of reactions with impurity elements. It is important that the components of the slag not contribute impurities to silicon which cannot be removed by later processing. MG silicon contains alkali and alkaline earth elements that are slag formers. An analysis was carried out to review the impurity elements and evaluate their propensity to go into the slag phase. This tendency is dependent on the acidity/basicity of the slag as well as the oxygen partial pressure. Table II shows the results of this analysis. Once again, refining by slagging is dependent on several parameters, viz., reaction kinetics, diffusion of impurities, partitioning coefficients, etc.

Gas blowing. During refining of molten MG silicon, gases can be purged through the melt. These gases can be of reactive nature to react with the impurity elements, or neutral to promote stirring of the melt. An advantage of a stirred melt is that it may limit the role of diffusion and promote reaction chemistry. Different gases have been used to promote reaction chemistry as well as promoting conditions for slagging and oxidation. The gases have also been used to carry solids (slags), liquids (moisture) or gases (gas mixtures) to react with molten MG silicon and promote refining.

Simultaneous reactions. Theoretical analysis of the above refining processes indicates that different experimental conditions may be necessary for refining different impurity elements; for some elements, refining is not an isolated process. Experimentally, combination of the refining processes has shown even better results compared to the sum of the individual processes. This may be explained by the fact that vigorous stirring of the "melt", "slag", "impurities" and "impurity species" are intimately mixed, thereby promoting reactivity and "tying up" the impurity, rather than its being restrained by diffusion. Similarly, impurities may be trapped in an oxidized state in the slag and removed thereafter by evaporation. Simultaneous reactions may allow complex, local equilibrium steps to happen sequentially which would otherwise not happen.

6. EXPERIMENTAL SETUP

Initial experiments using commercially available MG silicon were carried out with an experimental reactor modified for upgrading MG silicon. It was recognized that the ability to perform directional solidification, vacuum processing and scale up were important aspects of the processing unit for the experimental program. Therefore, experiments were shifted to using the largest Heat Exchanger Method (HEM) furnace. This furnace was modified to add the refining capability for upgrading MG silicon; the directional solidification and vacuum processing are already part of the HEM furnace. This unit can be used for charge sizes up to 450 kg and was used for much of the experimental program.

6.1 Experimental Reactor

During early stages an experimental reactor was set up for upgrading MG silicon in small charge sizes. It was intended to keep the reactor as a compact unit with the capability of refining MG silicon in the molten state and to extract samples from the molten bath from time to time. An induction coil was used as a heating source coupled to a graphite crucible. The graphite crucible also served as a retainer for a fused quartz crucible in which refining of MG silicon was carried out. Insulation was added to the furnace. The top section of the furnace had provision for inserting lances for gas flow and gas extraction, as well as adding powders to the molten bath. A provision was also made to achieve directional solidification of the charge after the refining experiments were completed. A schematic diagram of the bench-scale reactor modified to allow some directional solidification is shown in Figure 1. This reactor was used for the refining experiments up to approximately 1 kg charge sizes.

6.2 HEM Furnace

Based on initial experiments carried out with the experimental reactor, it was concluded that the achievable vacuum may not have been sufficient, and that the directional solidification was not adequate. It was also recognized that scale up in charge size will involve going to larger reactors; every time the reactor is changed new parameters would need to be stabilized. In view of these constraints, it was determined that an HEM furnace has the necessary features for the experimental program. The standard HEM furnace has the built-in features of good vacuum capability, one of the best directional solidification systems, a heat zone designed for silicon processing, and capability to use vacuum or controlled atmosphere. A schematic of the HEM furnace is shown in Figure 2. The largest HEM furnace, designed for commercial production of 69-cm square cross section silicon ingots, was selected for this project. This means that the same furnace could be used as the size of the ingot is increased. To accommodate the larger sizes, a round crucible can be used instead of the current square crucible, thereby allowing production up to 450 kg charges. All runs carried out in the modified HEM furnace are labeled as MG3-XX (where XX is the run #).

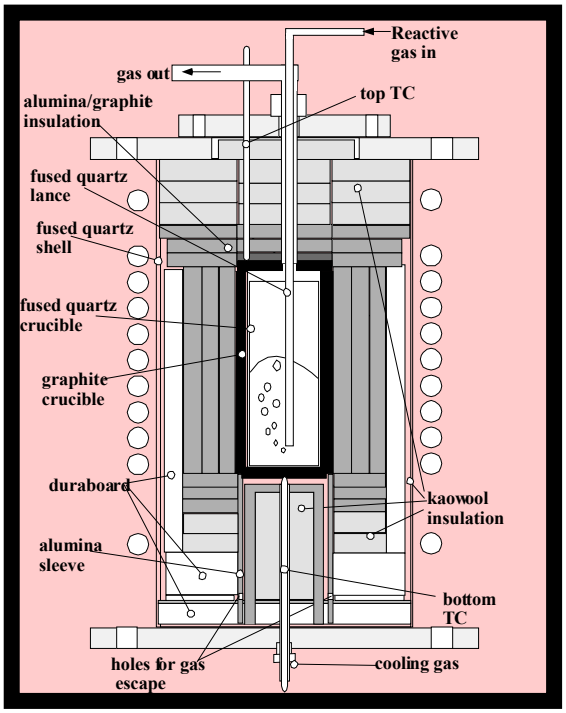

Figure 1. Schematic diagram of bench scale, modified to allow crude directional solidification.

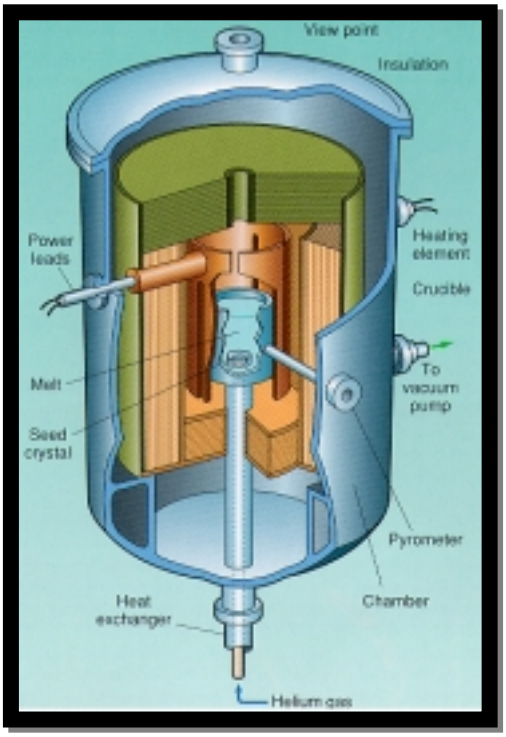

Figure 2. Schematic of an HEM furnace.

While the HEM furnace has all the features of silicon melting and directional solidification, it is normally used with high purity silicon meltstock. Therefore, this furnace had to be modified to add the refining capability to use it as a reactor for refining MG silicon. A schematic of the modified HEM furnace for the program is shown in Figure 3. This approach ensured that after the refining capability is added to the furnace, the technical feasibility of the project will be demonstrated in the shortest time, and then emphasis can be placed on scale up of charge size. The refining capability for upgrading MG silicon includes the ability to purge various reactive gases as well as argon gas through the furnace. The top cover plate for the HEM furnace was modified to add an observation window, a gas injection lance and sampling capability for taking samples from the melt on an as-needed basis.

One of the key ingredients of the refining step was the capability to handle reactive gases in a safe manner. The most difficult gas intended to be used for refining is hydrogen. An extensive number of safety features were analyzed to ensure that hydrogen can be used in an HEM furnace for refining at high temperatures and that the exhaust gases can be removed from the building in a safe manner. A burn-off option of the exit gases was incorporated so that no raw hydrogen is let into the building or in the exhaust system. Many discussions on the hazard operations were carried out and analyzed using operation personnel for the program, other CSI personnel and consultants. A simplified piping and instrumentation diagram to handle the gas flow and refining capability is shown in Figure 4.

The HEM furnace typically operates under a controlled atmosphere at a pressure of <1 atm. Therefore, changes were made to operate under flowing gases with a positive pressure. Appropriate safety features were added to the furnace so that it can be used in a positive pressure mode.

6.3 Crucibles for Refining Experiments

One of the important items in refining MG silicon is the crucible. It has to withstand the refining treatments, be compatible with silicon and the type of heating system, minimize contribution of impurities to the molten silicon, have capability for large size manufacture, and be low cost. Since all these characteristics are important, a task of the program was to evaluate low-cost crucible materials that can be used for refining of MG silicon. The types of crucible materials envisioned were alumino graphite, silicon carbide, silicon nitride, fused silica, mullite, zirconite and rammed silica crucibles.

A number of crucible manufacturers and suppliers have been contacted for data on crucibles available that could be utilized for refining of MG silicon. Some of the potential crucible materials are listed in Table IV along with some of the advantages and disadvantages. Most of the oxide materials were limited for use by the temperature capability and required support structure at the refining temperatures of molten silicon. The major problem encountered with most crucible materials was contamination of molten silicon. Only fused silica is available in high purity form and the reaction product with molten silicon is SiO, which is a volatile species and therefore removable from the heat zone. Almost all materials contained varying amounts of Al_2O_3, TiO_2, Fe_2O_3, free carbon and alkali oxides, all of which would contaminate molten silicon. Most of these materials are not available in very dense form and typically have porosity

of 10-33%, which makes these materials difficult to contain molten silicon. A limited number of materials are available in the very large sizes needed to contain up to 450 kg molten silicon, which is the goal of the program.

As discussed above, fused silica is the best crucible material available because of its high purity, minimal contamination on molten silicon, compatibility with silicon and availability in large sizes. Fused silica is available in crucible form in different shapes and sizes and using different raw materials and processing techniques. Therefore, various types of fused silica crucibles have been evaluated during the program for use for refining MG silicon. Some of the forms of fused silica crucibles are discussed below.

Clear Fused Silica Crucibles

These crucibles are produced using the arc fusion technique and are generally referred to as "snowball crucibles". Such crucibles are used in the Cz process, available routinely in sizes up to 24" diameter, and can be produced in even larger sizes on special order. One vendor of these crucibles has communicated that a slight variation of this process could produce crucibles up to 29" diameter x 78" high in size which could easily accommodate 1 metric ton of silicon.

Slip Cast Crucibles

Slip cast fused silica crucibles are also available in large sizes and have been used by Crystal Systems for the production of multicrystalline HEM silicon ingots for photovoltaic applications in sizes up to 69 cm x 69 cm square cross section. These crucibles can be produced in even larger sizes because of the simplicity of the slip casting process used in their manufacture.

Sand Fused Crucibles

In the manufacture of large crucibles, the materials cost becomes significant and it is necessary to reduce the raw material cost to allow low-cost production of crucibles. In this regard, high-purity silica sand is readily available and can be used for production of crucibles. One of the techniques for production of these crucibles is to fuse high-purity silica sand on an electrode and thereafter blow the sand onto a mold to produce a crucible. This technique was used in the United States to produce fused silica crucibles, but is no longer being utilized. A variation of this approach is to use an arc rod as a heating source and rotate a container of silica sand. The silica is fused around the container used as a mold. Such silica containers are being used by the chemical industry, and are available for use in MG silicon refining.

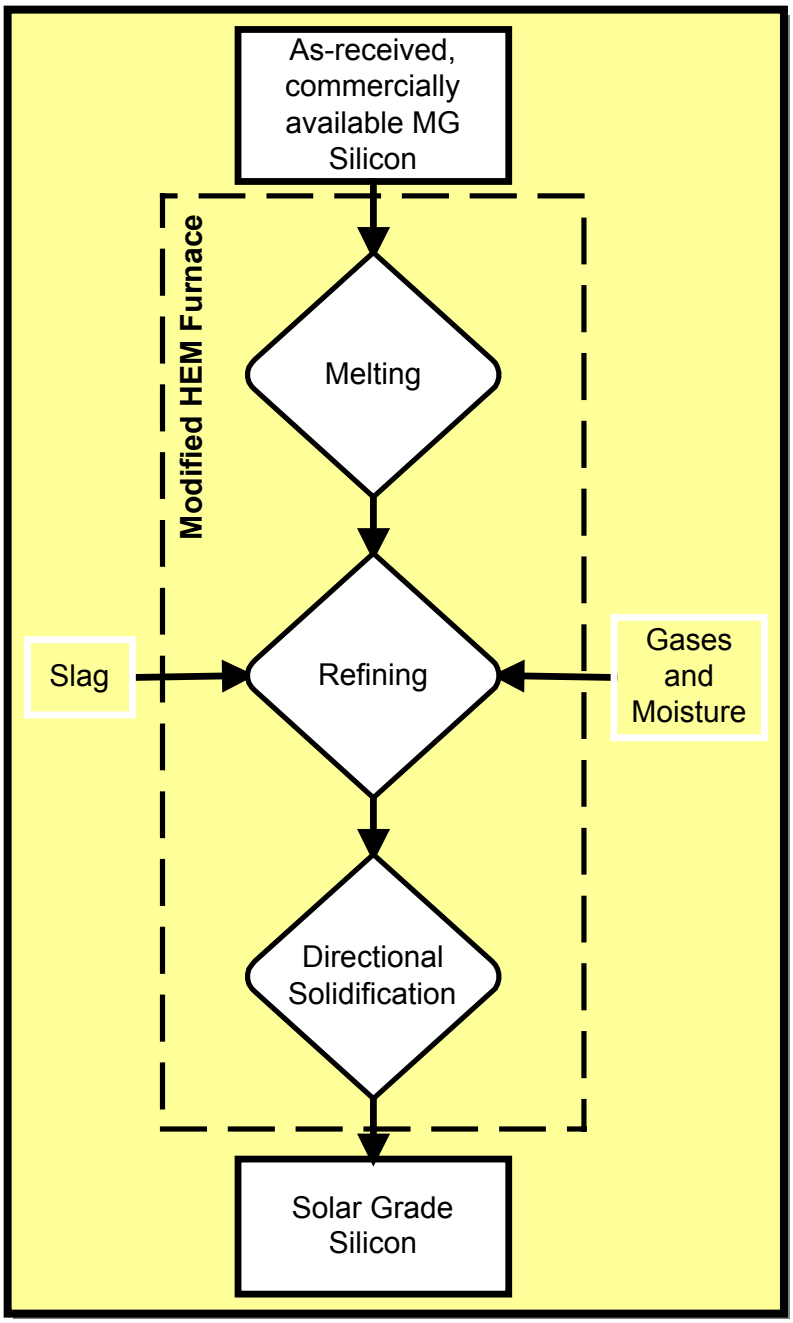

Figure 3. A schematic of the approach to upgrade MG silicon to SoG silicon using a modified HEM furnace for the program.

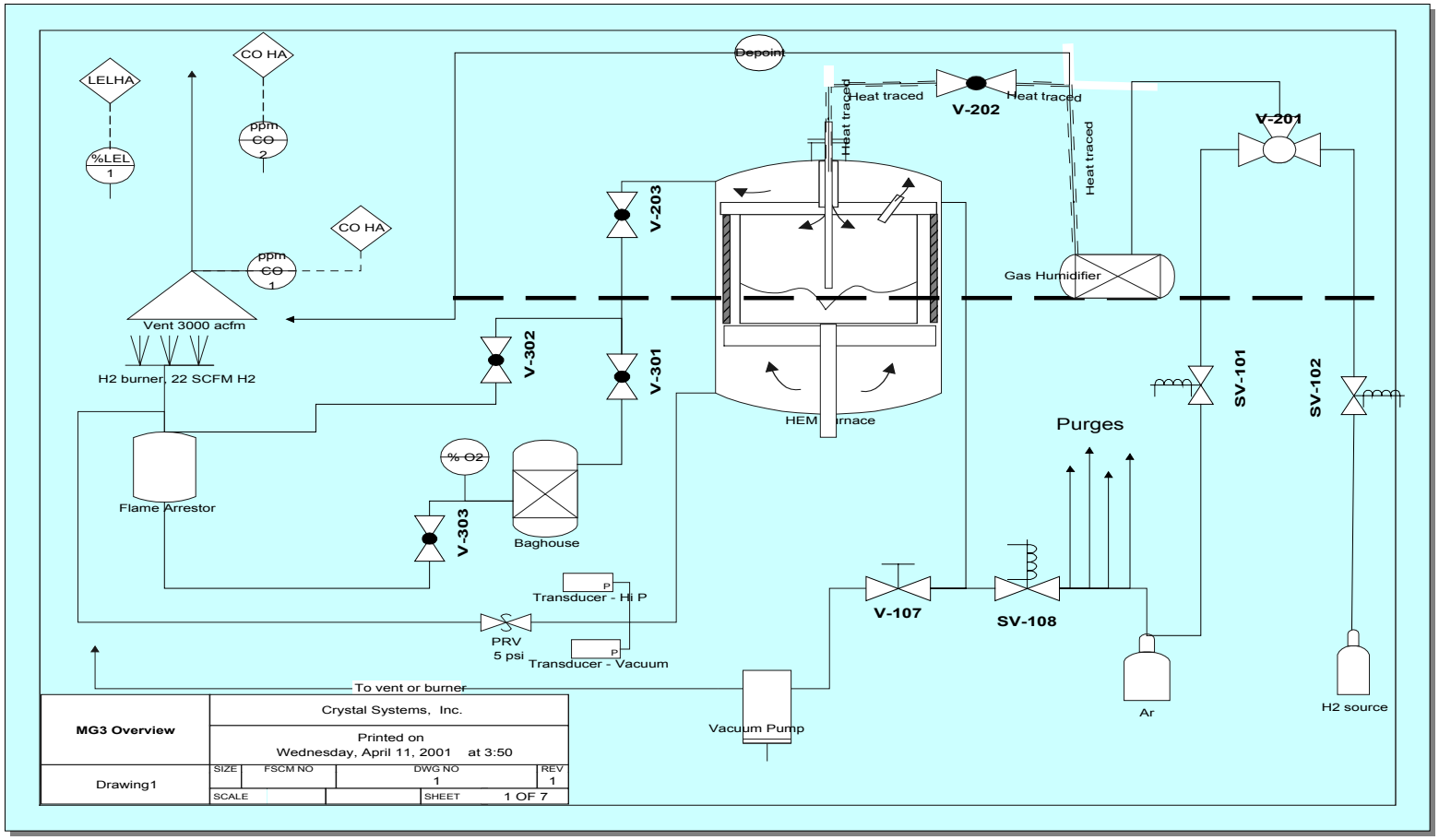

Figure 4. Overview of piping and instrumentation diagram for refining MG silicon using an HEM furnace.

Table IV. Comparison of crucible materials						
Crucible Material	Composition		Bulk Density gm/cc	Porosity %	Relative Thermal Shock Resistance	Problem
	Major	Other				
High Silica Crucibles	77%SiO_2	Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	1.7	26	Excellent	Contamination
High Silica Crucibles	85% SiO_2	Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	1.7	26	Excellent	Contamination
High Silica Crucibles	90% SiO_2	Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	1.7	26	Excellent	Contamination
High Silica Crucibles	99.8% SiO_2	Al_2O_3, TiO_2, Fe_2O_3	2.0	10	Excellent	Contamination
Semiconductor Grade Fused Silica	99.9% SiO_2	Minor	2.0	<10	Excellent	
Mullite	51% Al_2O_3	SiO_2, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	2.0	32	Fair	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	84% Al_2O_3	SiO_2, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	2.5	27	Good	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	88% Al_2O_3	SiO_2, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	2.6	27	Good	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	99% Al_2O_3	TiO_2, Fe_2O_3, K_2O, Na_2O	3.2	16	Fair	Contamination, Thermal Shock, Porosity
90% Zircon	63% ZrO_2	SiO_2, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	3.7	18	Good	Porosity
99% Zircon	67% ZrO_2	SiO_2, Al_2O_3, TiO_2, Fe_2O_3	3.5	18	Good	Porosity
Zirconia	97% ZrO_2	SiO_2, Al_2O_3, Ti_2O_3, Fe_2O_3, CaO, MgO	4.5	22	Fair	Contamination, Thermal Shock, Porosity
Silicon Carbide	72.5% SiC	SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O, Free Carbon	2.1	25	Good	Contamination, Porosity, Expensive
High Purity Silicon Carbide	98% SiC	Al, C, B, Ti, V, Zr, Fe	3.1	-	Good	B Contamination, Expensive
Clay Graphite	38% Carbon	SiO_2, Al_2O_3, SiC, TiO_2, Fe_2O_3, CaO, MgO, K_2O, Na_2O	1.7	24	Excellent	Contamination, Porosity
Magnesia	87% MgO	SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, K_2O, Na_2O	2.3	33	Fair	Contamination, Stability, Porosity
Silicon Nitride	Si_3N_4				Poor	Unstable in reducing atm, Stability, Purity, Expensive

7. EXPERIMENTAL RESULTS

Commercially available MG silicon, as received from the supplier and without any cleaning or surface treatments, was loaded in a fused silica crucible and placed in an experimental reactor or a modified Heat Exchanger Method (HEM) furnace for refining experiments. Initial experiments used about 1 kg MG silicon charge in the experimental reactor; later experiments were with 10 to 300 kg charge in the HEM furnace. Besides the capability of using larger charge sizes, the HEM furnace was set up with an improved vacuum capability and directional solidification. Refining experiments were carried out using different parameters, e.g.,

- degrees of vacuum as well as slight overpressure,
- different gas compositions,
- varying flow rates,
- slag components added to the charge initially or to the molten MG silicon,
- experimental conditions which were varied with time,
- the order in which the parameters were changed,
- lance diameter and height above bath,
- water content of gas,
- H_2 content of gas,
- temperature of molten silicon

7.1 Demonstrate feasibility using experimental reactor

A typical experiment involved heating the charge under vacuum until molten, stabilizing the melt at 1450°C, extracting the first sample, carrying out various refining steps with samples extracted after each step, evacuating the chamber after completion of refining steps, and directional solidification of the charge. Samples were extracted from molten MG silicon during refining using a suction bulb and a fused silica tube immersed in the molten silicon. Samples were also extracted from the directionally solidified ingot corresponding to the initial solidification stage and toward the end. These samples were analyzed using glow discharge mass spectroscopy, ICP emission spectroscopy and spark source mass spectroscopy. The results showed some effects due to the sample extraction technique, the ability to sample clean melt, entrapment of gases and secondary phases, inhomogeneities, simple directional solidification, etc. However, trends of refining with various parameters could be deduced from the data. The initially solidified ingot sample always showed a lower level of impurities, and samples toward the last solidified material showed considerably higher level of impurities. Details of experimental parameters for various runs are shown in Appendix A.

The emphasis of initial experiments was to develop refining procedures to reduce B and P in MG silicon. In this context results of Run # 3 (R014-98-CSI-003) are very significant. About 1 kg MG silicon charge was refined using moist hydrogen gas as the purge gas, and the charge was directionally solidified after refining. The gas flow rate and moisture content were varied; 15 samples were extracted and details of the experiment were reported[23]. The effectiveness of B removal during refining during Experiment #3 is shown in Figure 5, and the lowest level, obtained in the directionally solidified sample (# M17), was 0.68 ppmw (1.77 ppma). The biggest drop in B concentration in a single step of processing was in Run #4 (R014-98-CSI-004) where it dropped from 7.2 ppmw (18.69 ppma) to 0.013 ppmw (0.034 ppma). In this experiment vacuum processing did not lower the P concentration, as shown in Figure 6.

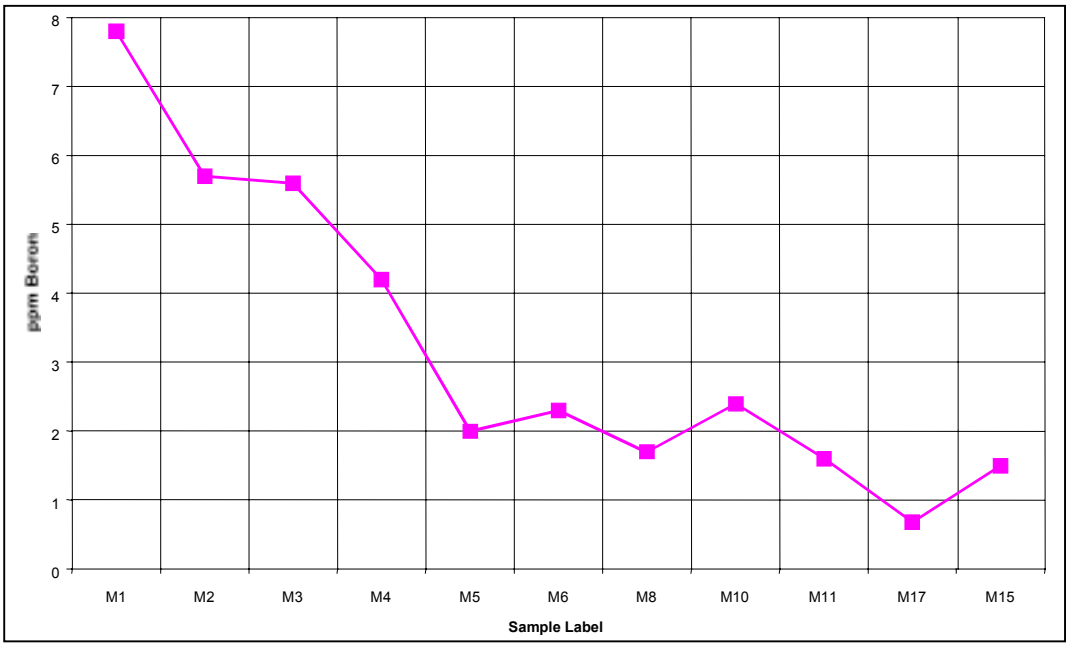

Figure 5. B reduction during refining of molten MG silicon in Experiment # 3.

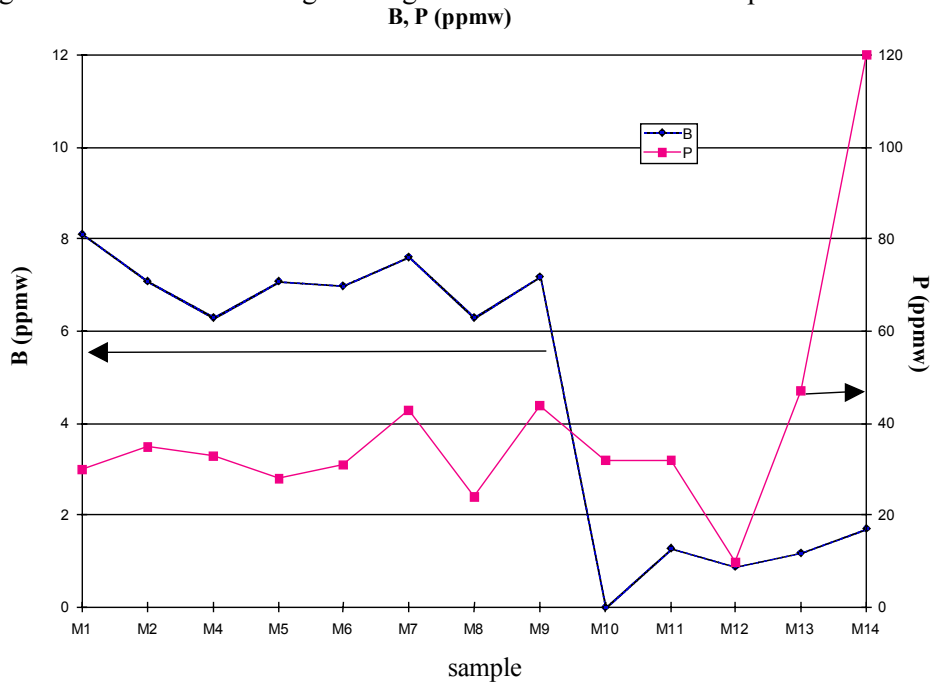

Figure 6. Effectiveness of B and P removal during refining of molten MG silicon in Run #4. Note the sudden drop in B in sample M10 and relatively no change in P concentration until directional solidification.

The data in Figure 6 was surprising in that the P concentration was not reduced during refining. It was reported[21] that P concentration can be reduced under vacuum processing. Later it was calculated that the vacuum obtained in the experimental reactor was not sufficient to reduce P concentration in MG silicon. Further experiments were therefore carried out using an HEM furnace, and the charge size was increased to a minimum of 25 kg.

7.2 Validate experimental reactor results using modified HEM furnace

Initial experiments using the modified HEM furnace were carried out to evaluate the effect of moist argon blowing (Run MG3-2), or vacuum and slagging (Run MG3-3). Better refining results were obtained when all refining procedures were carried out simultaneously (Run MG3-4). Thereafter, moist argon blowing and slagging were carried out under reduced pressure in the chamber to facilitate the removal of volatile reaction products from the chamber. The charge size was increased to 300 kg, but most refining procedures were developed on a 25 kg charge size.

Figure 7 shows the impurity analyses of several samples taken during the development of refining processes. In this experiment (MG3-7), a 25 kg MG charge was refined. The data was normalized to the first sample taken after meltdown of the charge. All elemental impurities except B and P are shown on a logarithmic scale, whereas B and P are shown on a linear scale on the right side. Significant refining was achieved. The directionally solidified silicon sample from this experiment is tabulated in Table V along with a similar sample for a 1 kg refined MG silicon charge. The 25 kg MG silicon ingot, after refining, shows impurity levels similar to the 1 kg sample; the refining times for both experiments were quite similar.

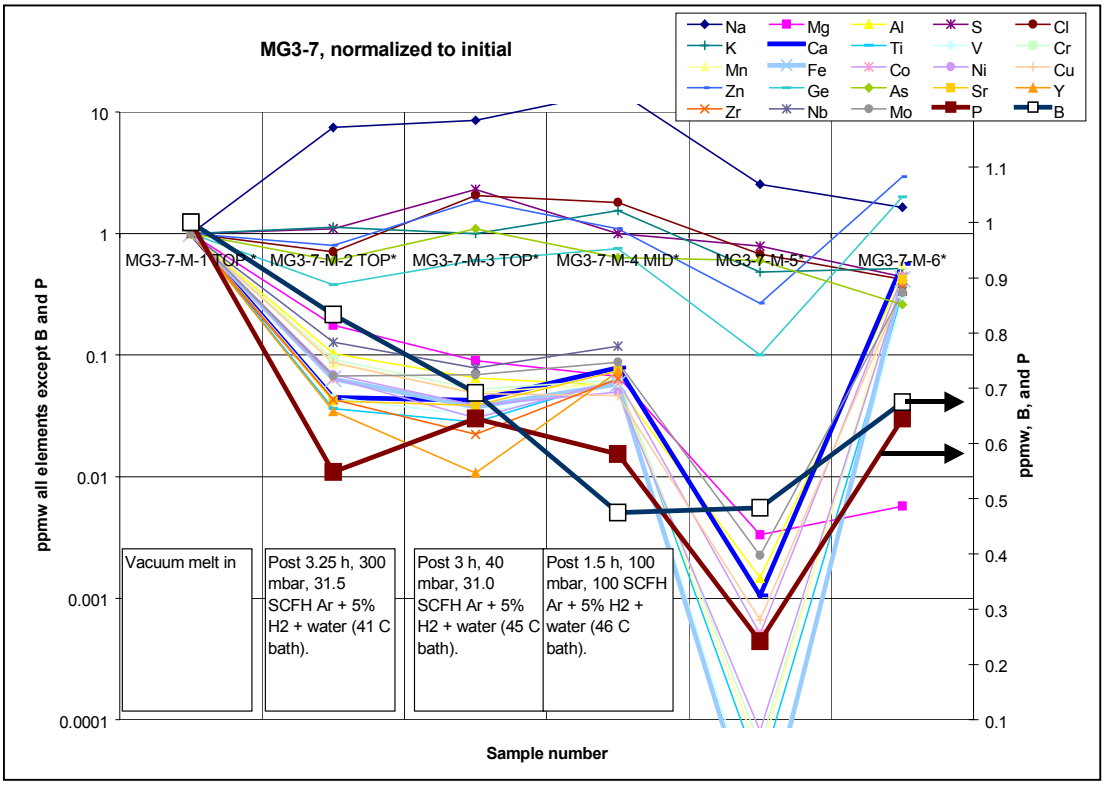

Figure 7. Impurity analyses of several samples taken during development of refining processes in Experiment MG3-7.

Table V. Impurity analysis (in ppmw and ppma) of MG silicon after refining followed by directional solidification.

Element	CSI-003 (1 kg Charge)		MG3-7-M-5 (25 kg Charge)	
	(ppmw)	(ppma)	(ppmw)	(ppma)
Li	0.01	0.040	0.011	0.045
B	0.68	1.77	5.8	15.1
Na	0.1	0.12	0.17	0.21
Mg	0.019	0.022	0.007	0.008
Al	2.5	2.60	2.5	2.6
Si	Major	Major	Major	Major
P	13	12	7.5	6.8
S	0.2	0.2	0.041	0.036
Cl	0.66	0.52	0.21	0.17
K	0.75	0.54	0.029	0.021
Ca	0.31	0.22	0.084	0.059
Ti	0.05	0.03	0.008	0.005
V	0.079	0.044	0.003	0.002
Cr	0.045	0.024	0.008	0.004
Mn	0.11	0.06	0.015	0.008
Fe	23	11.6	0.11	0.06
Co	0.07	0.03	0.004	0.002
Ni	0.21	0.10	0.021	0.01
Cu	0.12	0.05	0.04	0.018
Zn	0.029	0.012	0.02	0.009
Ge	1	0.4	0.2	0.08
As	0.58	0.22	0.18	0.07
Se	<0.5	<0.2		
Sr	<0.01	<0.003	<0.01	<0.003
Y	<0.01	<0.003	<0.01	<0.003
Zr	<0.01	<0.003	<0.01	<0.003
Nb	<0.01	<0.003	<0.01	<0.003
Mo	0.022	0.006	0.013	0.004
Ag	<0.5	<0.1	<0.5	<0.13
Cd	<0.3	<0.1	<0.3	<0.07
Sn	<0.05	<0.01	<0.05	<0.01
Sb	<0.05	<0.01	<0.05	<0.01
Ba	0.14	0.03	<0.01	<0.002
La	<0.01	<0.002	<0.01	<0.002
Ce	<0.01	<0.002	<0.01	<0.002
Pr	<0.01	<0.002		
Nd	<0.01	<0.002		
W	0.062	0.009	<0.01	<0.001
Pb	<0.05	<.01	<0.05	<0.007
Th	<0.005	<0.001	<0.01	<0.001
U	<0.005	<0.001	<0.01	<0.001

Run MG3-8 was carried out to expand the parameter space for Run MG3-7. A 25 kg MG silicon charge in a 33 cm square cross section crucible was heated slowly with silica powder. After the charge was molten, a sample from the molten bath was extracted. Thereafter, refining was initiated. The refining was carried out using moist argon and hydrogen gas through a lance. The bath temperature, gas flow and pressure in the chamber were varied, and samples were extracted from the molten bath for each parameter change. The list of the samples extracted during Run MG3-8 is shown in Table VI.

These samples were characterized by glow discharge mass spectroscopy, and the data for salient impurities are shown in Figure 8. It can be seen that significant reduction of impurities was achieved during refining and the lowest impurity levels were for sample MG3-8-M-7 corresponding to initial solidification after the refining step. The complete chemical analysis for all the impurities in sample MG3-8-M-7 is shown in Table VII. It can be seen that most of the impurities were significantly reduced and the B and P levels were 4 ppmw (10 ppma) and 7.4 ppmw (6.7 ppma), respectively.

Table VI. Details of experimental parameters and samples taken for Run MG3-8

Sample Name	Time	Processing	Comments
MG3-8-C-1	7/21/99 08:45	Post vacuum melt in.	Slag from bath surface.
MG3-8-M-2	7/21/99 10:15	Post vacuum melt in, and 1 hour hold at vacuum	3 attempts to get sample encountered slag layer. Instituted vacuum for 1 hour, then successfully obtained metal sample.
MG3-8-M-3	7/21/99 13:45	Post 2 hours 15 SCFH moist Ar + H_2 (28 C water bath), P = 20 mbar.	Good, unfractured sample.
MG3-8-M-4	7/21/99 16:17	Post 2 hours 31 SCFH most Ar + H_2 (40 C water bath), P = 45 mbar.	Good sample.
MG3-8-M-5	7/21/99 19:17	Post addition of 127 g silica, followed by 1.5 hours of 20 SCFH moist Ar + H_2 (55 C bath). P = 30 mbar.	Good sample quickly quenched.
MG3-8-D-6	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Dust from lance and inside of graphite sleeve.
MG3-8-M-7	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Beads collected from side of crucible – presumably pre-DS.
MG3-8-M-8	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Shards and chips from near bottom 1/3 of ingot.
MG3-8-D-9	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Dust from inside the graphite exhaust tube.

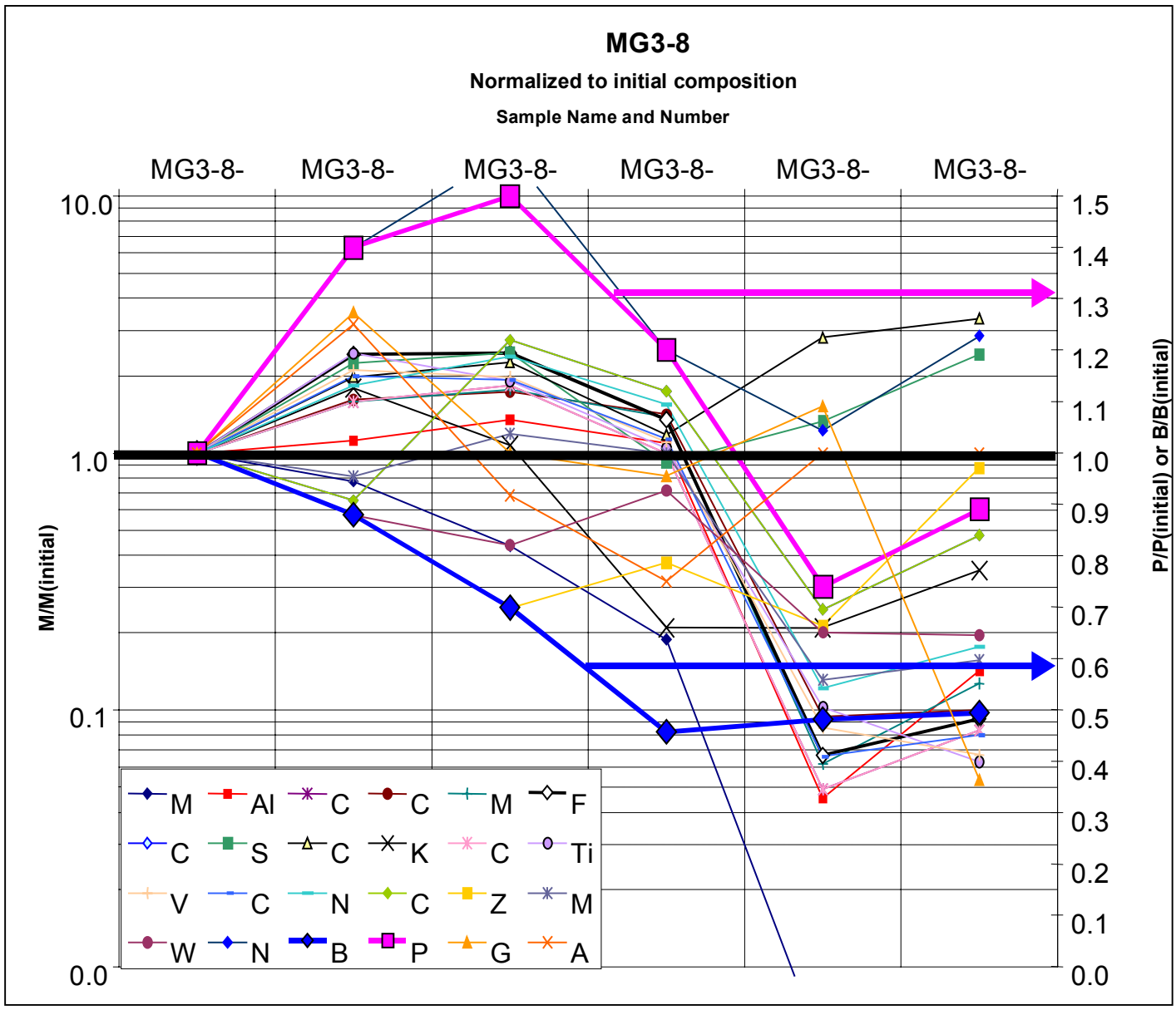

Figure 8. Impurity analysis for various samples in Run MG3-8. The data is normalized to initial composition to show effects of refining. Most impurities are shown using a log scale except for B and P, which are shown using a linear scale on the right side.

Table VII. Impurity analysis (in ppmw and ppma) using glow discharge mass spectroscopy for an initial directionally solidified sample from Run MG3-8

Element	MG3-8-M-7 (ppmw)	MG3-8-M-7 (ppma)
Li	<0.01	
B	4	10.4
Na	0.033	0.040
Mg	0.004	0.005
Al	16	17
Si	Major	Major
P	7.4	6.7
S	0.048	0.042
Cl	0.11	0.09
K	0.009	0.006
Ca	0.6	0.4
Ti	4.4	2.6
V	4.1	2.3
Cr	3.2	1.7
Mn	3.7	1.9
Fe	187	94
Co	0.099	0.047
Ni	5.1	2.4
Cu	1.7	0.8
Zn	0.2	0.07
Ge	2.4	0.9
As	0.12	0.04
Sr	<0.1	
Y	0.01	0.003
Zr	<0.5	
Nb	0.018	0.005
Mo	0.21	0.06
Ag	<0.5	
Cd	<0.3	
Sn	<0.05	
Sb	<0.05	
Ba	0.024	0.005
La	0.11	0.02
Ce	0.1	0.02
Pr	0.02	0.004
Nd	0.029	0.0056
W	0.42	0.06
Pb	<0.05	
Bi	<0.03	
Th	<0.01	
U	<0.01	

The element B is the most difficult to remove from silicon as it has a high segregation coefficient and has been difficult to remove using conventional processing techniques. In Run MG3-8, the B concentration was progressively reduced as shown by the plot in Figure 9. It can also be seen that no significant difference in B concentration was observed for directionally solidified samples, MG3-8-M-7 and MG3-8-M-8.

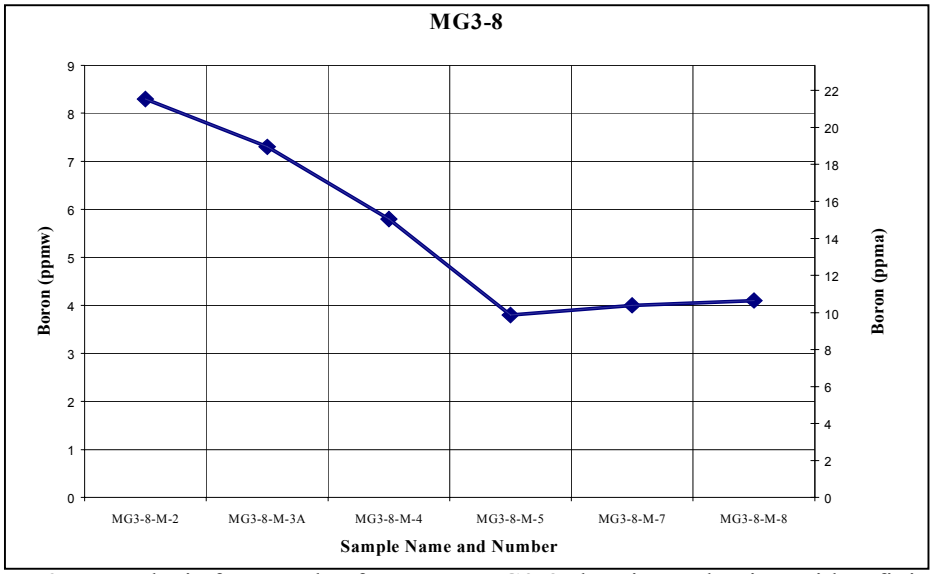

Figure 9. B analysis for samples from Run MG3-8 showing reduction with refining.

Run MG3-10 was carried out to refine a 60 kg metallurgical grade (MG) silicon charge in a 55 cm square cross section crucible. Silica powder was added to the meltstock during loading. The charge was heated overnight in the HEM furnace under vacuum. After the charge became molten, a sample was extracted from the molten bath. Thereafter, refining was initiated by blowing moist gases through the melt. The significant difference from earlier runs was to carry out refining using conditions that would prevent splashing of molten silicon during the refining operation. A number of chamber pressure, gas flow and moisture conditions and lance heights were tested. An extensive segment at ambient pressure was conducted as part of the experiment, and this allowed shakedown testing of new components of the off-gas system. At the end of each segment the chamber was backfilled and a sample was extracted. The details of the various segments and samples are shown in Table VIII.

After refining was completed, the heat zone was evacuated and the charge was directionally solidified and cooled to room temperature. A view of the ingot still in the crucible is shown in Figure 10.

Samples from initial solidification and from the last material to solidify were extracted from the ingot. All samples were analyzed for impurities using glow discharge mass spectroscopy. The data for all the samples normalized to the initial composition is shown in Figure 11. It can be seen that significant refining was achieved and the lowest impurities were in the initially solidified sample. Impurity analyses for this sample (MG3-10-M-10) are shown in Table IX. It can be seen that all the impurities were reduced significantly including B and P. The B and P concentrations were reduced to 4.1 ppmw (10.6 ppma) and 12 ppmw (10.8 ppma), respectively.

Table VIII. Details of the various segments and samples from Run MG3-10						
Sample Name	Seg. No.	Segment Duration (minutes)	Reactor Pressure (mbar)	Average Ar Flow (SCFH on air basis)	Average Dew Point of Gas T(C)	Comments
MG3-10-M-1			V	0.00	NA	good sample, analysis from top of sample (within 90 mm of top)
MG3-10-M-2	1	177	26.3	30.06	40.8	good sample, analysis from top of sample (within 90 mm of top)
MG3-10-M-3	2	118	118.4	29.26	45.3	good sample, analysis from uppermost 40 mm of sample
MG3-10-M-4	3	85	106	97.00	45.5	good sample, analysis from near 45 mm of top
MG3-10-M-5	4	119	297	123.40	48.5	good sample, analysis from 20 to 50 mm from top
MG3-10-M-6	Over-night hold	811	4		NA	good sample, analysis from within 70 mm of top
MG3-10-M-7	5	137	102.6	52.03	47.5	good sample, analysis from 20 to 40 mm from top
MG3-10-M-8	6	155	1021.7	128.95	48.7	good sample, analysis from 20 to 60 mm from top
MG3-10-M-9	7	110	125.1	65.00	48.7	good sample, analysis from 20 to 50 mm from top
MG3-10-M-10	DS early		8		NA	Center bottom of ingot. Total height less than 15 mm.
MG3-10-M-12	DS last		5		NA	Tip of late extrusion, top corner.
MG3-10-C-13	All					Off-gas duct ceramic and dust material.

Figure 10. A 60-kg MG silicon charge after refining during Run MG3-10.

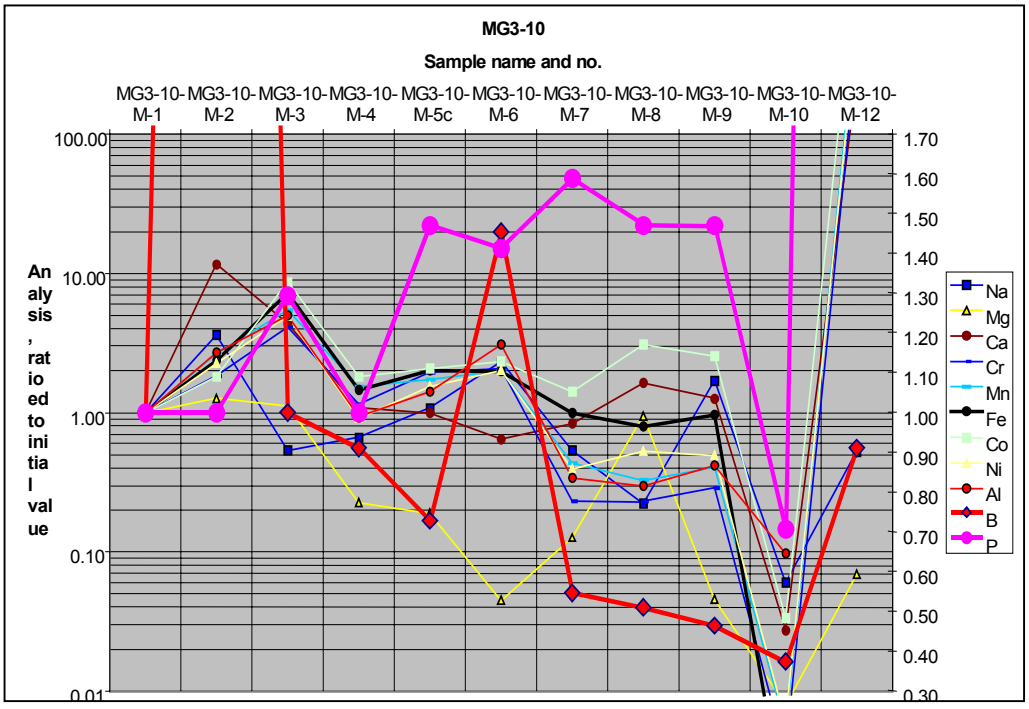

Figure 11. Impurity analysis for various samples in Run MG3-10. The data is normalized to initial composition to show effects of refining. Most impurities are shown using a log scale except for B and P, which are shown using a linear scale on the right side. The variable P may be due to slag inclusions in sampling.

Table IX. Impurity analysis using Glow Discharge Mass Spectroscopy for initial directionally solidified sample from Run MG3-10		
	MG3-10-M-10 (ppmw)	MG3-10-M-10 (ppma)
Li	0.015	0.061
B	4.1	10.6
Na	0.078	0.095
Mg	0.015	0.017
Al	20	20.8
Si	Major	Major
P	12	10.9
S	0.11	0.10
Cl	0.64	0.51
K	0.11	0.08
Ca	0.20	0.14
Ti	0.008	0.005
V	0.002	0.001
Cr	0.031	0.017
Mn	0.080	0.041
Fe	0.33	0.17
Co	0.005	0.002
Ni	0.065	0.031
Cu	0.030	0.013
Zn	<0.03	<0.01
Ge	<0.5	<0.2
As	0.30	0.11
Sr	0.031	0.010
Y	0.53	0.17
Zr	<0.01	<0.003
Nb	<0.01	<0.003
Mo	0.035	0.010
Ag	<0.5	<0.13
Cd	<0.3	<0.07
Sn	<0.05	<0.01
Sb	<0.05	<0.01
Ba	0.020	0.004
La	<0.01	<0.002
Ce	0.027	0.005
W	0.055	0.008
Pb	<0.05	<0.007
Bi	<0.03	<0.004
Th	<0.01	<0.001
U	<0.01	<0.001

A significant goal of the Phase I program was to reduce B and P concentrations to 10 ppma levels in a 50-kg charge. Experimentally, these levels were achieved with a 60-kg charge.

A significant result of Run MG3-10 was that the experimental procedures used did not cause splashing of molten silicon. This is important because splashing can reduce the silicon volume refined and destroy the heat zone, reduce efficiency of the operation and give erratic results. It was also an important step toward commercialization and further scale up of charge sizes.

7.3 Scale up of charge size for refining

Based on theoretical analysis and early experimental data the charge size was scaled up to 150 kg for refining[24-26]. For each experimental run, several segments were carried out with different parameters and a sample was extracted at the end of each segment. After the refining was completed, the molten silicon was directionally solidified. Samples were also extracted from the solidified ingot. All test samples were analyzed after the run was completed. The results showed that many impurities, other than B and P, were also removed during the refining step and were reduced even further during directional solidification. Typical impurities analysis for an experiment (#MG3-16) involving a 140 kg MG silicon charge is shown in Figure 12, and the impurities after directional solidification are shown in Table X. The data is presented as normalized to the initial composition in order to show effectiveness of refining. In some segments there was no refining or even contamination but finally most of the impurities, except B and P, were well below 0.1 ppma, and Al which was only slightly higher. Most of the B and P reduction was achieved during the refining step. From this data it is clear that all impurities in MG silicon, including B and P, were reduced during the refining step. The B and P were reduced to 3.3 ppmw (8.6 ppma) and 7 ppmw (6.3 ppma) respectively, and other impurities to 0.1 ppma level or below. It can also be surmised from the data that there was a steady reduction of B. In the case of P there was an overall reduction but, at times, it appeared that there was a reverse reaction operating which increased the P in silicon during a subsequent segment. In view of this result it was decided to concentrate on B reduction and to improve the effectiveness of the B reduction process.

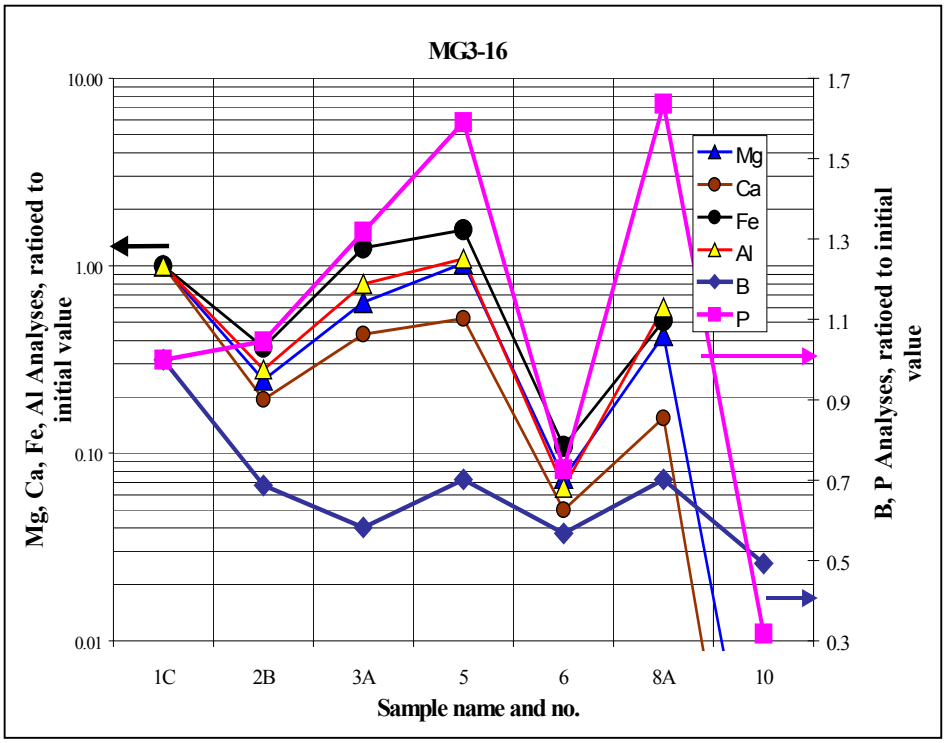

Figure 12. Impurity analysis for samples taken during refining of MG silicon. The data was normalized to initial composition. Impurities except B and P are shown in a logarithmic scale, and B and P are shown on a linear scale on the right side.

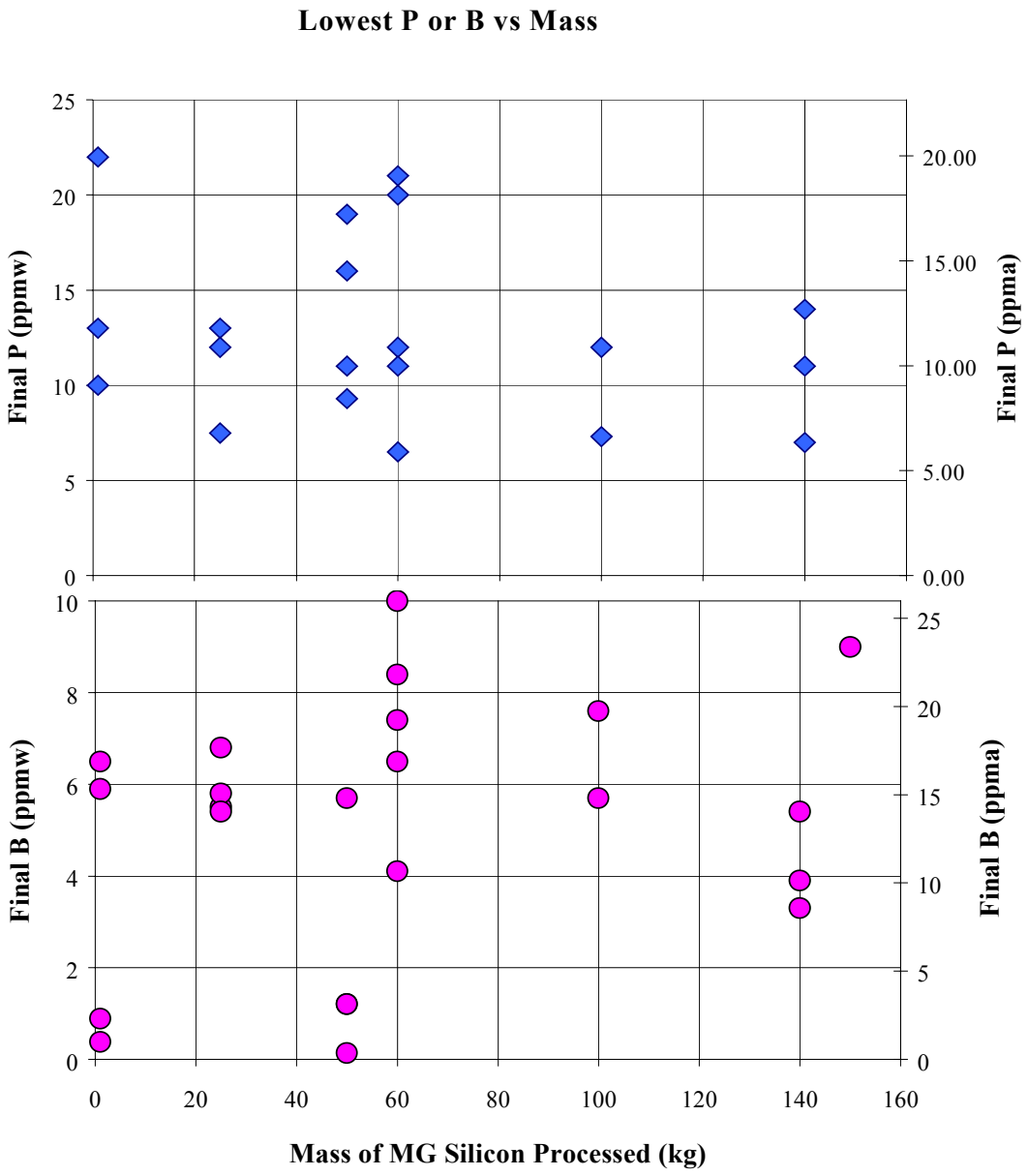

Figure 13. B and P concentrations achieved as a result of upgrading MG silicon for different charge sizes between 1 kg and 150 kg.

Table X. Impurity analysis from Sample #MG3-16-M-10 after directional solidification of a 140 kg MG silicon charge					
Element	MG3-16-M-10		Element	MG3-16-M-10	
	ppmw	ppma		ppmw	ppma
Li	<0.01	<.03	**Zn**	0.19	0.082
B	3.3	8.566	**Ge**	0.46	0.178
F	0.029	0.043	**As**	0.21	0.079
Na	0.003	0.004	**Sr**	<0.01	<0.003
Mg	0.004	0.005	**Y**	<0.01	<0.003
Al	0.16	0.166	**Zr**	<0.01	<0.003
P	7	6.341	**Nb**	<0.01	<0.003
S	0.008	0.007	**Mo**	<0.01	<0.003
Cl	0.064	0.051	**Cd**	<0.3	<0.075
K	0.016	0.011	**Sn**	<0.1	<0.024
Ca	0.051	0.036	**Sb**	<0.05	<0.012
V	0.016	0.009	**Ba**	<0.01	<0.002
Cr	0.009	0.005	**La**	<0.01	<0.002
Mn	0.013	0.007	**Ce**	<0.01	<0.002
Fe	0.13	0.065	**Pb**	<0.05	<0.007
Co	0.005	0.002	**Bi**	<0.03	<0.004
Ni	0.031	0.015	**Th**	<0.01	<0.001
Cu	0.046	0.020	**U**	<0.01	<0.001

Figure 13 shows the B and P concentrations achieved as a result of upgrading MG silicon for different charge sizes between 1 kg and 150 kg. As the charge size was increased, the B and P concentrations were reduced to similar levels showing very little sensitivity for refining with charge sizes.

7.4 Improve efficiency of B reduction process

Once it was clear that steady B reduction could be achieved during refining of MG silicon, emphasis shifted on improving the efficiency of the B reduction process. The efficiency of the B reduction for previous experiments was gauged using a linear model, directionally proportional model and square root model. On the basis of these models, refining times to bring the B concentration to <1 ppma level were estimated. Among these models, the linear model or the half-life model appeared to be more consistent with the data. Thereafter, this model was used. In addition to using MG silicon as feedstock, low resistivity B doped silicon was used for refining. Long refining segments were used along with iterative procedures to reduce the half-life for B reduction. Experiments MG3-19 and following experiments were undertaken with a view to reducing the half-life for B reduction. The results from Appendix I show that the half-life was reduced from many tens of hours to less than two hours. The final experiment #MG3-27 with MG silicon showed that B could be reduced to 0.1 ppmw (0.3 ppma). This experimental process resulted in a half-life of approximately two hours. A similar experiment was done with low-resistivity scrap silicon with B concentration approximately four to 10 times that of MG

silicon. A similar half-life was calculated. This material was used as feedstock for Cz and Fz growth and evaluated for solar cell performance.

7.5 Solar cell fabrication

Some of the samples from the refining experiment were used as feedstock for Fz and Cz crystal growth at NREL. Initial experiments with the refined MG silicon showed that it was not possible to produce dislocation-free single crystal using Fz. This was attributed to high carbon contained in the feedstock. A sample of the refined low resistivity B doped silicon material from Experiment MG3-28 was also used for crystal growth. Initial experiments with Fz showed that even though single crystal growth was initiated it turned multicrystalline. The material pulled by Cz was dislocation free and single crystal. Samples from the feedstock Fz and Cz crystals were characterized and used for fabrication of 1 cm x 1 cm solar cells, and the data is presented in Table XI. It can be seen that the feedstock material, Fz and Cz growth crystals, showed solar cell performance of 7.3%, 12.5% and 13.4%, respectively.

Sample	Source	ρ (Ω-cm)	Lifetime (μs) Early - Late	ρ (Ω-cm) After Anneal	Lifetime (μs) After Anneal Early - Late	Oxygen (cm-3) FTIR	Carbon (cm-3) FTIR
MG3-28-M-5D	As Received	0.33	0.9 - 0.3	0.44	0.3 - 0.2	6.E+17	4.E+17
FZ-010222	FZ from MG3-28-M-5B	0.44	133	0.45	3 - 4	<1E+17	4.E+17
CZ-010302	Baseline CZ	0.71	22 - 15	0.78/0.70	16 - 54	1.E+18	5.E+16
CZ-010309	CZ from MG3-28-M-5A	0.47	10 - 7	0.48/0.43	3 - 14	1.E+18	1.E+17

Anneal: 825C, 0.5 hours, followed by rapid cooling ("thermal donor anneal").
AR* = Antireflective Coating

7.6 Summary

Some of the conclusions that can be drawn at this stage, based on refining of commercially available MG silicon in the molten stage followed by directional solidification, are as follows:

- Commercially available MG silicon is an inhomogeneous product when analyzed for impurities in the ppm range. The purity level ranges from 98% to 99.7% and varies with suppliers and from batch to batch within the same supplier. Impurity levels (in ppma) for the MG silicon used for the experimental program were B 37-45, P 27-30, Al 600-1200, Fe 1000-3000.

- B reduction to 1.77 ppma was achieved in initial experiment with a 1 kg charge in the experimental reactor, using reactive gas with moisture content blowing through the charge and using a slag during refining,

- Evacuation, slagging, and moist argon gas blowing through the melt carried out separately did not effectively reduce the impurities in MG silicon; however, a combination of all significantly reduced the impurities,

- P reduction by evacuation of molten MG silicon at 1450°C was not effective with the present geometry, but with other refining steps P was reduced significantly,

- The refining procedures developed were used with charge sizes up to 150 kg,

- Hot loading of MG silicon was demonstrated to bring the charge size up to 300 kg,

- Impurities reductions by as much as 5 orders of magnitude were realized in experimental batches with the most problematic elements, B and P, showing refining by up to factors of 50,

- The procedures developed are consistent with scale up of charge sizes; they can be used in the present HEM furnace for refining charge sizes up to 450 kg,

- The HEM furnace is not designed for refining. Therefore, the reaction products cannot be easily removed from the furnace chamber, which may be the rate-limiting step for the overall refining reaction. Therefore, larger charge sizes (1-140 kg) were reduced to similar B and P levels using similar refining times,

- Experiments to improve the refining rates were carried out with 50 kg charge and B was reduced to 0.1 ppmw (0.3 ppma) after about 13 hours of refining yielding a half life of less than 2 hours,

- Similar results were achieved with low resistivity, B doped silicon containing 4 to 10 times the MG silicon B concentration,

- The B reduction time is dependent on starting B concentration and not on charge size,

- Refined low resistivity, B doped silicon was used as feedstock for Czochralski (Cz) and Float Zone (Fz) crystal growth and single crystal, zero dislocation structure was obtained,

- Solar cells (1 cm x 1 cm) fabricated from refined low resistivity silicon, Fz and Cz crystals were 7.3%, 12.5% and 13.4% efficiency, respectively,

- The refining procedures developed are simple processes which are scaleable and are not expected to add significant costs of refining; therefore, conversion of MG silicon to SoG silicon should result in low-cost added value,

- The B half-life model can predict the refining time for given experimental processes.

8. SCENARIO FOR LARGE SCALE PRODUCTION

The present program was initiated based on research and development experiments carried out during early 1980's using an HEM furnace with 3 kg charge. It was demonstrated that all impurities, including B and P, could be reduced to <1 ppm level by refining commercially available MG silicon in the molten state followed by directional solidification. Initial experiments during the current program were carried out using an experimental reactor and 1 kg charge to duplicate the earlier experiments, and it was demonstrated that B could be reduced to 1.77 ppma by reaction with moisture, gas blowing through the charge and using a slag during refining. It was recognized that B and P have to be reduced by refining and other impurities could be reduced by directional solidification. Since directional solidification was a key process it was decided to use an HEM furnace with one of the best directional solidification systems. Modifications were made to incorporate refining capability prior to directional solidification.

It was essential to concentrate on reducing B and P during refining. Therefore, different procedures were used to evaluate refining of impurities. These procedures involved reaction with moisture, gas blowing, slagging, etc. Data gathered from these experiments showed that B concentration could be reduced steadily by reaction with moisture and gas blowing. However, P concentration was usually reduced with refining, but was quite sensitive to the experimental variables. It appeared that, in addition to the forward reaction to reduce P, sometimes the back reaction was also operating so that there was no systematic decrease of P. Therefore, a separate step for P reduction may be required and may involve slagging. Emphasis therefore shifted to improving the efficiency of B reduction. It is felt that the basic design of the HEM furnace for directional solidification may be limiting the completeness of reactions to remove B and P from molten silicon. The reaction products are not easily removed from the furnace chamber thereby promoting the reverse reaction.

In view of the results achieved, it is clear that an effective B reduction process has been developed. In the semiconductor industry, large amounts of heavily B doped material is available as scrap that cannot be utilized in its present form by the photovoltaic industry. The combination of availability of this surplus material and the B reduction process developed could be exploited to have an additional source of silicon feedstock available to the photovoltaic industry to produce modules in the range of 100-200 MW on an annual basis. Meanwhile, an alternate refining furnace can be designed so that the reaction products can be removed from the furnace chamber. An effective P reduction process should be developed that can be utilized for MG silicon in combination with the B reduction process. At that stage prototype manufacturing of SoG silicon can be initiated by refining commercially available MG silicon. This material can be made available to the photovoltaic community as a second step to the refined high B doped silicon. The photovoltaic community can adapt appropriate ingot growth systems and solar cell fabrication to be compatible with using these new feedstocks.

The next stage could be development of a ladle with an auxiliary heating source whereby molten silicon from an arc furnace in an MG silicon production plant can be poured directly into this ladle and refined, followed by directional solidification. The photovoltaic community can then

be supplied this material as feedstock for evaluation. Depending on the requirement, the charge of molten MG silicon could be diverted for refining into SoG silicon. A typical MG silicon production furnace generates about 1.5 tons of silicon every hour. Therefore, substantial amounts of SoG silicon can be supplied to the photovoltaic industry without the need of setting up a special facility or special MG silicon production furnaces. As the requirement of the SoG silicon increases, changes can be made to the arc furnace and purity of feedstock used in the arc furnace to improve the quality of MG silicon production. This scenario therefore offers the lowest cost without the necessity of setting up special facilities to produce SoG silicon. The procedures developed are all compatible with the operation of an MG silicon production plant. The estimated cost of SoG silicon in the production environment of an MG silicon plan is $10/kg.

8.1 Estimate of production costs

This analysis assumes that a "heated ladle" is used for converting MG silicon to SoG silicon in a MG silicon production plant. Typical costs of production of MG silicon are about $1/kg. In this scenario molten MG silicon from the arc furnace is tapped directly into the "heated ladle" refining system at the rate of 1 ton of molten MG silicon per tap. The molten MG silicon is refined for B removal using moist gas blowing, slagged for P removal and then directionally solidified for reducing all other impurities.

A 36-hour cycle time assumes the following sequence:

Tapping of molten MG silicon	1 hour,
B removal using moist gas blowing	8 hours,
Slagging for P removal	8 hours,
Directional solidification	15 hours,
Charge removal and prep for next run	4 hours

Total cycle time	36 hours

Assuming a plant size of 1000 tons/year production about 6 "heated ladle" type refining systems will be required. The costs of these systems and infrastucture will be about 4 million dollars. The costs of molten MG silicon is assumed at $2/kg; the additional costs are to pay for indirect costs associated with SoG operation in a MG silicon plant. The variable costs for direct labor, overhead, feedstock, crucibles, gases, slags, expendables, electricity, etc. for the 1000 ton SoG plant are about $7.6 million per year, or $7.62/kg of SoG feedstock. The cost contribution of the various elements of variable costs is as follows:

Direct Labor for refining	$0.90
Ancillary labor	$0.45
Overhead	$0.45
Feedstock	$2.50
Crucibles	$1.25
Gases	$1.13
Slags	$0.13

Expendables	$0.25
Electricity	$0.32
Misc.	$0.25
Total variable costs	**$7.62**

The production of SoG silicon is compatible with the processing of MG silicon. Therefore, it can be carried out without the expense of setting up a plant specifically for the production of SoG silicon. As the demand for SoG increases more and more MG silicon can be diverted for production of SoG silicon.

9. CONCLUSIONS

Development of SoG silicon feedstock is the most important problem facing the photovoltaic community so that the projected growth of the industry can be maintained. The most direct approach is to upgrade MG silicon so that a nearly inexhaustible supply of feedstock can be developed and the dependence on the electronics industry is curtailed. The present program was to upgrade commercially available MG silicon by reducing B and P in the molten state followed by directional solidification. This approach was based on research and development results carried out on small charge sizes. After initial feasibility demonstration, the charge size was increased to 300 kg. The refining procedures developed included reaction with moisture, gas blowing, slagging, etc., consistent with processes used in an MG silicon production plant. Refining from 1 to 150 kg charge sizes showed that a simple moist gas blowing operation reduced the B level from 20-60 ppma to <1 ppma and the P level from 20-60 ppma to <10 ppma. After it was demonstrated that effective B reduction could be achieved, emphasis was placed on reducing the time of refining. These experiments were carried out with approximately 50 kg charge size, and B was reduced to 0.3 ppma with a half-life of <2 hours. The B reduction process was also tested on low-cost silicon scrap available from the semiconductor industry that contained significantly higher B concentration, 50-400 ppma. Using this material as feedstock, the B concentration was reduced to <1 ppma. This refined material was used as feedstock for the Fz and Cz crystal growth. The Fz crystal was twinned and turned multicrystalline, whereas the Cz crystal was single and dislocation free. Test solar cells of 1 cm x 1 cm size fabricated at NREL demonstrated 7.3%, 12.5% and 13.4% efficiency for as-received, Fz and Cz grown crystals using this refined material.

Development of a simple B reduction process to reduce 20-60 ppma B in commercially available MG silicon to 0.3 ppma is considered a technical breakthrough toward development of an SoG silicon. Good progress has been made toward reducing P concentration from 20-60 ppma in MG silicon to about 7 ppma. However, it is necessary to reduce the P level to <1 ppma. Most of the other impurities have been reduced to <0.1 ppma. The processes developed during the program are consistent with practices used in MG silicon production plants. Therefore, this technology, after development, could be easily adapted in an MG silicon production plant. The projected cost of producing SoG silicon by upgrading MG silicon is $7.62/kg, which is less than the goal of $20/kg. In addition, this approach does not require the capital expenditure to set up a dedicated SoG silicon production plant.

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13. ABSTRACT *(Maximum 200 words)* This report summarizes the results of the developed technology for producing SoG silicon by upgrading MG silicon with a cost goal of $20/kg in large-scale production. A Heat Exchanger Method (HEM) furnace originally designed to produce multicrystalline ingots was modified to refine molten MG silicon feedstock prior to directional solidification. Based on theoretical calculations, simple processing techniques, such as gas blowing through the melt, reaction with moisture, and slagging have been used to remove B from molten MG silicon. The charge size was scaled up from 1 kg to 300 kg in incremental steps and effective refining was achieved. After the refining parameters were established, improvements to increase the impurity reduction rates were emphasized. With this approach, 50 kg of commercially available as-received MG silicon was processed for a refining time of about 13 hours. A half life of <2 hours was achieved, and the B concentration was reduced to 0.3 ppma and P concentration to 10 ppma from the original values of 20 to 60 ppma, and all other impurities to <0.1 ppma. Achieving <1 ppma B by this simple refining technique is a breakthrough towards the goal of achieving low-cost SoG silicon for PV applications. While the P reduction process was being optimized, the successful B reduction process was applied to a category of electronics industry silicon scrap previously unacceptable for PV feedstock use because of its high B content (50-400 ppma). This material after refining showed that its B content was reduced by several orders of magnitude, to ~1 ppma (0.4 ohm-cm, or about $5x10^{16}$ cm^{-3}). NREL's Silicon Materials Research team grew and wafered small <100> dislocation-free Czochralski (Cz) crystals from the new feedstock material for diagnostic tests of electrical properties, C and O impurity levels, and PV performance relative to similar crystals grown from EG feedstock and commercial Cz wafers. The PV conversion efficiency of 1-cm^2 devices made from Cz crystals grown using the new feedstock were 95% as high as those from Cz crystals grown using EG feedstock and were comparable to those we obtained using commercial <111> Cz wafers. Devices with an efficiency of 7.3% were also made directly on wafers cut from the feedstock that had not gone through a controlled directional solidification. Only a few cells have been processed. Device parameters for this material have not yet been optimized, and additional diagnostic device fabrication, analysis, and verification is under way. The successful B treatment process developed during the program can be used with high-B-doped silicon scrap from the electronics industry thereby making available, for the short term, a new silicon feedstock for an additional 200 MW/year annual production of PV modules. For the future, this approach, when used in an MG silicon production plant, will produce SoG silicon for $7.62/kg, which is less than the goal of $20/kg.

14. SUBJECT TERMS: PV ; heat exchanger method furnace ; solar grade ; metallurgical grade ; Czochralski crystals ; high-B-doped silicon ; directional solidification ; mass spectroscopy ; large-scale production

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