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SEQUENTIAL PURIFICATION AND CRYSTAL GROWTH FOR THE PRODUCTION OF LOW COST SILICON SUBSTRATES

Annual Report, September 15, 1979—September 14, 1980

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Solar Energy

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ANNUAL REPORT
FOR PERIOD
15 SEPTEMBER 1979 - 14 SEPTEMBER 1980

MING LIAW, FRANK SECCO D'ARAGONA

PREPARED FOR

UNITED STATES
DEPARTMENT OF ENERGY
DIVISION OF SOLAR TECHNOLOGY
AND
SOLAR ENERGY RESEARCH INSTITUTE

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1. INTRODUCTION

The objective of this program is to identify and develop low cost processing for fabricating large grain size polycrystalline silicon substrates. Metallurgical grade silicon (MG-Si) which is low cost and abundant for industrial usage was chosen as starting material. However, MG-Si cannot be used directly as substrates for solar cell fabrication for the following reasons: (1) It contains 1 to 2% metallic impurities. The metallic impurities are regarded as minority carrier lifetime killers. Furthermore, even if the MG-Si is used as substrates for thin film solar cells, the metals with a high diffusivity in silicon can rapidly outdiffuse to the active region of the epitaxial layer and degrade the solar cell performance. 2) It is produced as irregular shapes with a fine grain structure. Both irregular shapes and fine grain structures are not adequate for solar cell applications. Therefore, the further purification and recrystallization of MG-Si is needed.

The conventional method of purifying MG-Si requires the conversion of Si to gaseous chlorosilanes. Chlorosilanes are purified by distillation. The purified chlorosilanes are then converted back to elemental silicon using a chemical vapor deposition process. Purified polysilicon requires recrystallization to form for electronic device or solar cell applications.

Various purification techniques have been reported in the literature¹⁻⁵. The techniques being studied under this program use direct methods for the purification of MG-Si. The process uses sequential steps of purification followed by crystal growth. The steps of sequential purification include: (1) leaching of MG-Si charge, 2) phase separation of non-soluble impurities from molten silicon, 3) reactive gas treatment of molten silicon, 4) liquid-liquid extraction (called slagging), and 5) impurity redistribution using ingot pulling. All the purification steps, with the exception of step (1), are performed in a consecutive manner using a crystal puller. The purified ingots will be produced in a desired ingot dimension and further recrystallization is not necessary.

In this report we will present the theory and experimental results for each purification technique. The relative effectiveness of the various steps will be assessed and the most important step(s) will be recommended. Finally the electrical characteristics of solar cells built on a thin epitaxial layer deposited on single pulled MG-Si substrates will be discussed and compared to single crystal substrates.

2. PURIFICATION BY ACID LEACHING

2.1 Theoretical Considerations

In the literature the term acid leaching has been referred to as a method for silicon purification. Strictly speaking, leaching is the extraction of constituents from a solid material using a percolating liquid. Since silicon can not be permeated by any acid solution, "chemical etching" may be a more appropriate term than "acid leaching".

The commercial-metallurgical grade silicon (MG-Si) is produced by the reduction of molten sand (SiO_2) using charcoal in an arc furnace. The molten silicon is rapidly solidified after discharge from the arc furnace. During the solidification the impurities with a low segregation coefficient will be rejected from the solidifying grains. The liquid which is rich in impurities will eventually be trapped inside the grain boundaries. The chemical leaching is aimed to dissolve the impurities existing in the grain boundaries.

The effectiveness of the impurities removal by acid leaching is therefore determined by the grain size of the MG-Si. Ideally each grain should consist of a single crystal of silicon. For this reason MG-Si was pulverized to small particles prior to the acid leaching experiment.

2.2 Experimentals

The leaching of MG-Si has been studied using the following variables: (i) time of leaching and (ii) leaching solution.

We have studied in particular the leaching by hydrochloric acid and by hot aqua regia. A quantitative study was made by measuring the impurity concentration in the HCl and aqua regia solution by atomic absorption and in the MG-Si by emission spectroscopy.

2.2.1 Hydrochloric Acid Leaching

For the HCl experiments we have used MG-Si granules about 3 mm in diameter having a nominal Fe and Al content of 0.5% and 0.2% respectively. Figure 1 shows the impurity concentration (in ppm wt) in the HCl solution (31% HCl) vs the time of leaching as measured by atomic absorption. The experiment was conducted at room temperature. The weight ratio of MG-Si to HCl solution was 1 to 24. The figure shows that the concentration of Al, Fe, Cu and Mn in the HCl solution increases with the time of leaching. The rate of leaching in the range of 0.1 to 15 ppm wt/hr was observed in the first four hours of leaching. Further leaching gave only a slight increase in concentration. The total amount of impurities removed is insignificant as compared to that in the original MG-Si. Consequently, the change in concentration of the Al, Fe, Cu and Mn in the solid MG-Si was undetectable by emission spectroscopy. It also shows that the concentration of Ca and Mg are not affected by the HCl leaching.

2.2.2 Aqua Regia Leaching

For the aqua regia experiments pulverized MG-Si was used. It had a nominal Fe content of 1% and particle size between 75 and 250 μm . Leaching was done at a temperature of 75-80°C using an aqua regia to silicon ratio of 5 to 1 by weight. Figure 2 shows that the concentration of Ca, Mn and especially Al in the aqua regia solution increases very rapidly within the first two hours of leaching. The rate of leaching varies from 3 ppm/hr for Cu to 400 ppm/hr for Al. After the first two hours

Figure 1. Impurity concentration in HCl solution versus time of leaching.

Figure 2. Impurity concentration in aqua regia solution versus time of leaching.

the concentration levels off and does not seem to increase with time.

A semi-quantitative analysis of the impurity concentration in leached MG-Si was also made by the emission spectroscopic method. Figure 3 shows the plot of concentration of impurities remaining in MG-Si as a function of leaching time. After 24 hours of leaching, fresh aqua regia was used to replace the aged solution. This is indicated in Figure 3 as first and second cycle. Figure 3 clearly shows that no significant amount of impurities had been removed after two hours of leaching even with the use of fresh aqua regia. However, it has to be pointed out that the emission analytical results given here were only semi-quantitative and the accuracy may not be better than $\pm 50\%$.

3.0 PURIFICATION AND PHASE SEPARATION

3.1 Physical Separation of Insoluble Impurities

A considerable amount of impurities insoluble in the molten MG-Si are always observed as shown in Figure 4 (a). The presence of the slag on the melt surface prevents the growth of an ingot with a uniform diameter, high purity and large grain size.

A technique has been developed to remove this insoluble phase. The slag is manipulated to aggregate at the center of the crucible by combining a gas flow which is directed onto the crucible wall with the crucible rotation. The gas directed onto the crucible wall will force the slag to move away from one side of the crucible. By adjusting the crucible rotation rate, the crucible will complete one revolution of rotation before the slag flows to the opposite side of the crucible wall. This will blow the slag back to the center. Once the slag is aggregated at the center of the melt, the temperature of the furnace is decreased to supercool the melt. A single crystal seed is dipped through

Figure 3. Impurity concentration in MG-Si versus time of leaching.

Figure 4 (a). Slag floating on molten MG-Si.

Figure 4 (b). Clean surface of molten MG-Si after slag removal.

the slag to contact the melt. Silicon melt starts to freeze on the seed together with the majority of slag which is trapped by the freezing melt. After the slag has been trapped, the quick withdrawal of the seed will remove the slag from the melt. Figure 4 (b) shows a photograph of the MG-Si melt after the removal of the slag. Figure 5 shows the solidified slag separated from the melt.

The reduction of impurities from MG-Si by the phase separation was studied by the comparison of impurity concentration in the original MG-Si with that in the removed slag. Table 1 lists the results analyzed by emission spectrographs and shows that the Fe and Al concentrations in the slags are much higher than those in the original MG-Si. No quantitative data can be given because of the lack of standards at that concentration range. Other impurities such as Ga, Sr, Zr and Mg in slags were 10 times greater than in the original MG-Si. This suggests that the concentration of these impurities in MG-Si melt became much lower than in the starting MG-Si. The concentration of Mn and Co was found 3 times higher in the slags than the original MG-Si.

The non-soluble impurities were also separated from MG-Si upon melting a large quantity in a crucible. The separation resulted from the sedimentation of the impurities which have a greater density than silicon melt. Figure 6 (a) and (b) compare the top and bottom surfaces of the frozen MG-Si in a quartz crucible. A layer of sand-like impurities on the bottom surface of the frozen MG-Si is clearly seen.

3.2 Vacuum Treatment

3.2.1 Theoretical Consideration

The purpose of applying a vacuum to a crystal puller which contains a MG-Si charge is to enhance evaporation of impurities in silicon. Evaporation may occur in two stages. The first is during the heating of the MG-Si charge prior to melting. The second is

Figure 5. Slag attached to seed.

TABLE I

COMPARISON OF IMPURITY CONCENTRATIONS (%) IN SLAGS AND
IN ORIGINAL MG-Si ANALYSIS BY EMISSION SPECTROSCOPY

	<u>M-G Si</u>	<u>Slag 1</u>	<u>Slag 2</u>
Cr	.033	.010	.010
Ca	.010	>>.10	>> .10
Sr	.00033	.033	.01
Mn	.033	.010	.010
Al	.10	>>.10	>> .10
Fe	> .10	>>.10	>> .10
Ni	.0033	.0033	.0033
Co	.00033	.001	.001
Zr	.001	.010	.010
Ti	.033	.033	.010
Cu	.001	.001	.001
Be	10^{-4}	10^{-4}	10^{-4}
V	.01	.010	.010
Mg	10^{-4}	.010	.010
B	.001	.00033	.00033

FIGURE 6 (a) The Top Surface of a Frozen MG-Si.

FIGURE 6 (b) The Bottom Surface of a Frozen MG-Si.

the evaporation from the molten solution after the silicon charge has melted. The rate of evaporation of elemental impurities from a solid charge is primarily determined by the vapor pressure of the impurity. Table II lists the relationship between the vapor pressure and temperature of impurities contained in MG-Si. Column 3 of Table II shows that at one atmosphere Cl, P, K, As, Cd, Na and Mg boil at a temperature below the melting point of silicon (1412°C). When a vacuum is applied and the pressure is reduced to 10^{-4} atmosphere, the boiling point of the impurities is decreased as shown in Column 2. It also shows that at this pressure the additional impurities, Ca, Sb, In, Mn, Ga, and Al boil at a temperature below the melting point of Si. Thus the purification of MG-Si can be improved by applying a vacuum to a heated MG-Si charge.

Table II also lists the impurities of low vapor pressure, which can hardly be removed by evaporation. These elements are the transition metals, Mo, Zr, B and C. Fortunately these impurities (with the exception of B) have a very low segregation coefficient and can be easily removed by an ingot pulling technique.

Evaporation of impurities from molten silicon is not simply related to their vapor pressure. Other thermodynamic constants are needed to predict the volatility of the solute from a molten solution. For a dilute liquid solution of an impurity in silicon, the variation of impurity concentration due to evaporation in a vacuum can be expressed as⁶:

TABLE II
BOILING POINT ($^{\circ}\text{C}$) OF THE IMPURITIES OF CONCERN IN
MG-Si AS FUNCTION OF TWO VAPOR PRESSURES

	<u>10^{-4} ATm</u>	<u>1 ATm</u>
Cl	-134	-34
P	23	280
K	261	779
As	290	622
Cd	312	765
Na	350	914
Mg	516	1126
Ca	688	1482
Sb	752	1617
In	1077	2167
Mn	1087	2097
Ga	1227	2427
Al	1272	2327
Cu	1412	2595
Si*	1467	2477
B	1477	2527
Fe	1564	2735
Ni	1657	2837
Ti	1717	3127
Co	1827	3097
V	2067	3527
Zr	2177	3577
Mo	2727	4804
C	2897	4502

$$\frac{dCl}{dt} = - \frac{AEC_l}{W_l} \quad (1)$$

where: A = area of evaporation surface
 Cl = concentration of impurities
 W_l = weight of molten silicon

$$\text{with: } E = \frac{\beta M_s}{\sqrt{2} \pi MRT} \exp \frac{(\overline{\Delta H} - \Delta G^0)}{RT} \quad (2)$$

where: β = constant
 M_s = molecular weight of silicon
 M = molecular weight of impurity
 $\overline{\Delta H}$ = partial molal heat of solution
 ΔG^0 = molal free energy of evaporation
 R = gas constant
 T = absolute temperature

Equations (1) and (2) show that the evaporation rate is primarily determined by the difference between the partial molal heat of solution and molal free energy of evaporation $(\overline{\Delta H} - \Delta G^0)$. The values of ΔH and ΔG^0 for some impurities in molten silicon are listed in Table III. The smaller the negative value of $(\overline{\Delta H} - \Delta G^0)$, the smaller the value of E^{-1} . The calculated E^{-1} for these impurities are also given in Table III. The smaller the E^{-1} value the greater the evaporation rate from the molten silicon solution. Note that the sequence of E^{-1} values for various impurities, (i.e., $Sb < As < In < Ga < Mn < Al$ etc.) is different from that of the boiling point of impurities ($P < As < Sb < In < Mn < \text{etc.}$)

3.2.2 Vacuum Treatment in a Multiple Zone Furnace

MG-Si has been heat treated at 1350°C under a vacuum for the evaporation study. These experiments were carried out under Motorola's in house project⁷. Figure 7(a) shows

TABLE III

ESTIMATED VALUES OF $\overline{\Delta H}$, ΔG^0 and E^{-1}
FOR SOME IMPURITIES AT THE MELTING
POINT OF SILICON (after Ref.6)

ELEMENT	$\overline{\Delta H}(\text{K}_{\text{cal}})$	$\Delta G^0(\text{K}_{\text{cal}})$	E^{-1}
P	-50	+18	5×10^3
As	-34	+16	1×10^2
Sb	- 5	- 2	6
In	- 1	- 1	1×10^2
Mn	-10	-10	2×10^3
Ga	- 1	-21	4×10^2
Al	- 4	-28	5×10^3
Cu	- 3	-31	1×10^4
B	-10	-34	1×10^5
Fe	+ 6	-42	2×10^4

Figure 7. (A) Apparatus used for vacuum evaporation experiments, (B) Temperature profile of the deposition zone and elements deposited on the various zones.

the sketch of the apparatus used for this study. A MG-Si charge was contained in a 4" diameter closed-bottom quartz tube. The extension of the quartz tube was reduced to 2" in diameter and contained a free space. The quartz tube was placed in a multiple zone furnace with a temperature profile shown in Figure 7(b). When the MG-Si charge was heated at a vacuum of 10^{-3} torr, impurities evaporated from the MG-Si and condensed on the inner wall of the upper quartz tube. A few hours of heat treatment resulted with deposition of a continuous layer of film on the 550°C to 1100°C temperature zone. The film deposited in each temperature zone exhibits a characteristic metallic luster.

Samples of deposited film were taken with a given increment of length along the axis of the quartz tube. The emission spectrographic technique was used to identify the impurities in the deposited film. Figure 7(b) lists the impurities. The position of the row listing the impurities is approximately the same as the position shown in Figure 7(a) from which the samples were taken. By comparison of the elements listed in Figure 7(b) with the boiling point data shown in Table II, it can be seen that the majority of the vacuum deposited film is consisted of elements with a low boiling point. However, the elements with a high boiling point (B, Ti, and Fe) have also been found in Figure 7(b). It suggests that these impurities may also exist as volatile compounds in MG-Si.

As indicated in Section 3.2.1 vacuum evaporation may be a potential technique for removing some impurities from molten MG-Si. In the present experiment we have subjected MG-Si nuggets to reduced pressure both in the solid and molten states.

3.2.3 Vacuum Treatment in a Crystal Puller

Following initial pumpdown to a vacuum of 0.5 torr power was applied to the furnace to heat up the MG-Si charge. There was immediately a vacuum deterioration probably due to interstitial H_2O outgassing.

Outgassing persisted however as the temperature was increased well above the boiling point of H_2O , indicating that some volatile impurities were leaving the charge. The original vacuum was eventually restored in about an hour at temperature close to the melting of silicon. The increased pressure during heating corresponds to the evaporation of impurities as demonstrated in Section 3.2.2. When all the silicon was melted it started to boil vigorously almost immediately; at the same time the surface of the melt was getting progressively cleaner. In 5-10 minutes the slag had completely disappeared. At this time, since the furnace was not equipped for vacuum growth, the furnace had to be backfilled with Ar and a pull rod with the seed inserted into the chamber before regular growth could take place. The experimental results indicate that the vigorous boiling of molten silicon can splash the floating impurities off the melt surface. Figure 8(a) shows the slag floating on the silicon melt. Figure 8(b) shows the melt boiling with some slag still left. Finally, Figure 8(c) shows a slag-free melt ready for an ingot growth. The impurity concentrations at the seed and tang ends of a vacuum-slagged MG-Si ingot are listed in Table IV. For comparison the impurity concentrations in an ingot in which the slag was removed by physical means is also shown.

There seems to be a reduction by a factor of 3 for some transition metals and Al, with the notable exception of Fe. Although these results seem encouraging, the impurity concentration reduction obtained by vacuum-treating the silicon melt is not high enough, especially in the light of the close relationship between grain size and impurity concentration, to be of any significance. Nevertheless, the method seems to be a viable alternative to the removal of slag by physical means.

(a)

(b)

(c)

Figure 8. Disappearance of slag from MG-Si melt by vacuum treatment

- (a) Slag on MG-Si melt
- (b) Melt boiling
- (c) Melt free of slag

TABLE IV

COMPARISON OF IMPURITY CONCENTRATION IN MG-Si
INGOTS PULLED FROM MELTS PURIFIED BY:

(A) VACUUM TREATMENT OF SLAG

(B) PHYSICAL SEPARATION OF SLAG

<u>ELEMENT</u>	(A) VACUUM TREATMENT PRIOR TO INGOT GROWTH		(B) SLAG REMOVAL BY PHYSICAL MEANS	
	<u>MG-190(S)</u>	<u>MG-190(T)</u>	<u>MG-192(S)</u>	<u>MG-192(T)</u>
CR	10	100	100	330
CA	1	33	10	100
SR	<5	<5	<5	5
MN	10	100	100	330
AL	100	330	330	1000
FE	≥1000	>1000	>1000	>1000
NI	≤5	10	10	33
CO	<5	5	5	10
ZR	<10	10	<10	33
TI	10	100	33	100
CU	≤1	33	10	33
BE	<1	<1	<1	<1
V	<5	<33	10	33
MG	<1	<1	≤1	≤1
B	<10	<10	<10	<10
SN	<5	<5	<5	<5

4. PURIFICATION BY REACTIVE GAS TREATMENT

4.1 Theoretical Consideration

4.1.1 Reaction of Cl_2 , SiF_4 and H_2O with Metals

The conceptual approach in this study is to expose the molten silicon to reactive gaseous species and form volatile products containing impurities that escape the melt. In order to react preferentially with impurities rather than with silicon the free energy formation (or reaction) of the impurity compound(s) should be more negative than that of silicon compound(s). A survey of the free energy of formation of compounds has been made. The elements used for this argument are the primary impurities in MG-Si.

Reaction of chlorine with metals

The values of the above free energy of formation are for a temperature of 1500°C . Since the values of ΔF for listed chloro-compounds are greater than that of SiCl_4 , it suggests that chlorine or chlorine containing gases would be good choices to be used as reactive gases.

Reaction of SiF_4 with metals

The above values of the free energy of reactions for a temperature of 1700°K . The last two equations suggests that SiF_4 may be a good choice for the reaction with B and Al.

Reaction of $\text{H}_2\text{O}(\text{g})$ with metals

$\text{H}_2\text{O}(\text{g})$ seems to be able to react preferentially with boron and aluminum over silicon.

4.1.2 The Volatility of Compounds

The volatility of reaction compounds has been surveyed. Table V lists the temperatures at which the compounds reach the vapor pressure of 10 mm and 760 mm. It can be seen that all the metal chlorides or fluorides are more volatile than molten silicon with the exception of AlF_3 . Oxides, however, are relatively non-volatile. It is anticipated that the metal chlorides or fluorides resulted from the reaction between reactive gas and metal impurities may probably escape from the silicon melt.

4.2 Experimental

4.2.1 Treatment with HCl and SiF_4

The reactive gases, HCl and SiF_4 have been used for treatment of molten silicon. The arrangement of apparatus is shown in Figure 9. Electronic grade HCl and reagent

TABLE V

LIST OF TEMPERATURES ($^{\circ}\text{C}$) AT WHICH THE COMPOUNDS
REACH THE VAPOR PRESSURE OF 10 mm or 760 mm

<u>COMPOUND</u>	<u>10 mm</u>	<u>760 mm</u>
AlCl_3	123.8	180.2
AsCl_3	23.5	130.4
CdCl_2	656	967
FeCl_3	235	319
MgCl_2	930	1418
NiCl_2	759	987
BCl_2	-66.9	12.7
FeCl_2	700	1026
MnCl_2	778	1190
SiCl_4	-34.4	56.8
BF_3	-141	-110
AlF_3	1224	1537
SiO_2	1732	2227
Al_2O_3	2385	2977

Figure 9 The method of sequential treatment of Molten Si with various reactive gases.

grade SiF_4 were used. Each reactive gas was diluted with He or Ar prior to bubbling into silicon melt.

In each experiment silicon melt size was 4.0 kg.

The total volume of the reactive gas bubbled into silicon melt was calculated from the flow rate and the time of bubbling. The temperature of silicon melt was slightly higher than its melting point to prevent freezing during the reactive gas treatment.

During the bubbling of either HCl or SiF_4 a vigorous chemical reaction occurs with the melt. The reaction product was formed as smoke and prevented the clear view of the melt surface.

After the melt was treated with a reactive gas the residual insoluble impurities floating on the melt surface were removed by a physical means as described in section 3.1. An ingot was pulled from the melt. The impurity analytical data were taken from both the pulled ingots and the melts remaining in the crucibles.

The distribution of impurities in the solidified silicon is not uniform. The location of the sample taken can affect the analytical result greatly. Effort has been made to take the sample in a consistent method:

Two samples were taken from the seed and tang ends of the pulled ingots.

Two samples were also taken from the solidified melt remaining in the crucible. They are the portions which froze at the very first and the very last.

Table VI summarizes the analytical results for the ingots pulled from the melts treated with 0, 1.5 $\%$, 3.54 $\%$, 4.5 $\%$, and 7.08 $\%$ HCl. The numbers without parentheses are the concentration analyzed by spark source mass spectroscopy.

TABLE VI

COMPARISON OF IMPURITY CONCENTRATION (PPM wt) IN SILICON
INGOTS FROM THE MELTS TREATED WITH VARIOUS AMOUNTS OF HCl.

Element	No HCL	SEED END OF INGOTS (Polygonal structure)		TANG END OF INGOTS (lamellar structure)				
		1.5l HCL	4.5l HCL	No HCL	1.5l HCL	3.54l HCL	4.5l HCL	7.08l HCL
Cr	<5	<5	<5	100	33	33	33	33
Ca	<1	<1	<1	3.3	3.3	--	1	<1
Sr	<5	5	<5	<5	<5	--	<5	--
Mn	<1(.04)	<1(.63)	<1(.08)	100(370)	100(290)	100	100(370)	100
Al	<5(60)	<5(36)	<5(60)	330(3300)	330(900)	300	330(3300)	100
Fe	<2(.13)	<2(2.4)	<2(.13)	>1000(840)	>1000(560)	1000	>1000(840)	1000
Ni	<5(.45)	<5(.53)	<5(.45)	33(19)	33(19)	30	33(19)	10
Co	<5	<5	<5	10	10	10	10	<10
Zr	<10	<10	<10	10	10	30	10	--
Ti	<1(.08)	<1(.25)	<1(.04)	330(210)	330(120)	100	330(160)	100
Cu	<1(.02)	<1(.02)	<1(.01)	3.3(150)	3.3(.33)	3	1(.67)	1
Be	<1	<1	<1	<1	<1	--	<1	--
V	<5	<5	<5	100(91)	100(91)	30	100(25)	30
Mg	<1(.15)	<1(.27)	<1(<.10)	10	3.3	<10	3.3	--
B	<10(.42)	<10(.18)	<10(.64)	<10	<10	<10	<10	3

Note: (1) HCl was bubbled into Kg Si melts

(2) Figures listed in parentheses are measured by spark source mass spectrographs

At the seed end of the ingots the analytical results obtained by the emission spectroscopy show that the concentration of all elements is below the detection limit of the analytical technique. A better detection limit was seen from spark source mass spectroscopy (SSMS). However, no correlation can be found between the impurity concentration and amount of HCl treatment to the silicon melt. Some effect of HCl has been seen at the tang end of ingots. The emission spectrographic results show that the concentration of Cr, Ca, Mn, Ti and Cu was slightly decreased by HCl treatment. The results from SSMS only show the reduction of Cu concentration.

The concentration of impurities in the melts remaining in the quartz crucible is shown in Table VII. The concentration of Cu, Zr and Ti in the first frozen melts was decreased by a factor of 3 to 10 by the treatment with HCl. However, an increase in the concentration of Cr, V and B was seen. The concentration of Ca and V was decreased in the last frozen melt by the treatment with 7.08 g HCl.

Table VIII shows the emission spectrographic results for an ingot pulled from the melt treated with SiF_4 . SiF_4 used in this run was 0.15% of Si. When the comparison is made between the impurity concentration at the tang end of ingots pulled from the treated and non-treated melts (shown in Table VI) the concentration of Cr, Ca Mn and Ti and V was lower in the treated sample by a factor of 3 to 10.

In the patent literature¹, it has been claimed that molten silicon can be purified by treatment with a mixture of halogen-containing gas and oxygen or steam. The halogen-containing gas can be a halogen (X), HX , SiX_4 , or $\text{SiH}_x\text{X}_{4-x}$. It has been demonstrated that some

TABLE VII

COMPARISON OF IMPURITY CONCENTRATION (PPM wt) IN SILICON MELTS TREATED WITH VARIOUS AMOUNTS OF HCl*

Element	FIRST FROZEN MELTS			LAST FROZEN MELTS		
	No HCl	3.54 l HCl	7.08 l HCl	No HCl	3.54 l HCl	7.08 l HCl
Cr	30	100	100	100	100	300
Ca	10	<1	1	30	30	<1
Sr	<1	<1	<1	<1	<1	<1
Mn	100	300	300	300	1000	300
Al	1000	1000	1000	300	1000	1000
Fe	>1000	>1000	>1000	>1000	>1000	>1000
Ni	30	100	30	100	1000	100
Co	<10	30	10	30	100	30
Zr	100	30	30	300	300	30
Ti	100	30	30	300	>1000	1000
Cu	10	100	100	30	1000	300
Be	--	--	--	--	--	--
V	100	<30	>1000	300	300	100
Mg	<1	<1	<1	<1	1	<1
B	--	10	10	--	30	3

* A 4 Kg Si Melt was Used

TABLE VIII

IMPURITY CONCENTRATION (PPM wt) IN THE SILICON
INGOT PULLED FROM A SiF₄ TREATED MELT

<u>ELEMENT</u>	<u>SEED</u>	<u>MIDDLE</u>	<u>TANG</u>
Cr	< 5	10	10
Ca	<1	<1	<1
Sr	<5	<5	<5
Mn	<10	33	33
Al	<5	100	100
Fe	<2	1000	1000
Ni	<5	33	10
Co	<5	5	5
Zr	<10	33	33
Ti	<1	100	33
Cu	<1	<1	<1
Be	<1	<1	<1
V	<10	33	33
Mg	<1	<1	<1
B	<2	<2	<2

metallic impurities were reduced by approximately a factor of 3 in concentration. The present work using HCl or SiF₄ produces similar results. This seems to agree with the thermodynamic data that the free energy of formation of the impurity halides is slightly more negative than that of silicon halides and that the vapor pressure of the impurity halides is higher with the exception of AlF₃.

4.2.2 Treatment with H₂/H₂O

An experiment has been performed on a 2 Kg weight melt after removing the slag from the melt. H₂ gas (5% H₂, 95% Ar) was bubbled through a 40 - 45°C water bath as shown in Figure 9. The flow rate of the gas was approximately 0.1 cu ft /hr. The total time for the gas bubbling into the MG-Si melt was 6 minutes. An ingot was then pulled from the melt for the impurity analysis. Table IX shows the comparison of impurity concentration in silicon ingots pulled from melt with and without treatment of H₂/H₂O. It shows that the concentration of Al and Mn in the treated melt were respectively one-half and one-third of those in the non-treated melt. However, some of the impurities such as Cu, C, Ca and B show higher concentration in the treated melt.

4.2.3 Treatment with H₂/H₂O + Cl₂

A study was also made on the treatment of molten MG-Si by H₂/H₂O and followed by Cl₂. The melts were made from 1-pulled ingots. Table X shows the results. The total amount of H₂ (5%) bubbled into Si melt for the experiment listed in Column (B) was 0.03 Cu. ft. The total amount of H₂/H₂O and Cl₂ (47 PPM) bubbled into the melt for the experiment listed in Column (C) was respectively 0.06 cu.ft. and 1.2 cu.ft. A melt size of 2 Kg was used. Table X shows that the concentration

TABLE IX

COMPARISON OF IMPURITY CONCENTRATION
(PPM wt) IN SILICON INGOTS PULLED FROM
MELTS WITH AND WITHOUT TREATMENT OF H_2/H_2O .

<u>ELEMENT</u>	<u>NO TREATMENT</u>	<u>H_2/H_2O TREATMENT</u>
Cd	< .16	< .16
Cu	.02	.04
Ni	< .029	.83
Fe	< .09	< .09
Mn	.46	.16
Ti	< .02	< .02
Ca	.05	.20
P	.74	.74
Al	22.0	12.0
C	.17	.83
B	.90	1.30

TABLE X

COMPARISON OF IMPURITY CONCENTRATIONS
(PPM wt) IN SILICON MELTS TREATED WITH
AND WITHOUT H_2/H_2O OR $H_2/H_2O + Cl_2$

ELEMENT	(A)	(B)	(C)
	NO TREATMENT	TREATED WITH H_2/H_2O	TREATED WITH $H_2/H_2O + Cl_2$
Cu	<10	<10	<10
Ni	30	<10	<10
Fe	>1000	1000	1000
Mn	300	100	100
Ti	300	100	100
Al	300	100	100
B	<10	<10	<10
Cr	100	30	30
V	100	30	30
Zr	<10	<10	<10
Co	<10	< 10	<10

of Mn, Ti, Al, Cr and V were reduced by one-third by the treatment of H_2/H_2O or $H_2/H_2O + Cl_2$. However, no difference was seen between the treatment of H_2/H_2O and $H_2/H_2O + Cl_2$.

5.0 PURIFICATION BY SLAGGING

5.1 Theoretical Consideration

Slagging is based on the principle of liquid-liquid extraction. This technique has been used in the steel industry. The slag used to extract impurities in the molten silicon should fulfill the following criteria:

- (a) It should be immiscible with molten silicon.
- (b) Its melting point should be approximately equal to the melting point of silicon.
- (c) It should not contaminate the silicon melt.
- (d) It should have a greater chemical affinity to impurities than to silicon.

In order to fulfill the first criterion, oxide slags were chosen. Among them the oxides of the transition metals or heavy metals were excluded for consideration. The alkali earth oxides seemed to be worth consideration. Since a quartz (SiO_2) crucible is used for containing the silicon melt, the oxide added into the crucible inevitably forms mixed oxides with the quartz. Figure 10 shows the phase diagram of the $CaO-SiO_2$ system. The system has two eutectic points. There is one at 46 atomic percent SiO_2 with eutectic temperature at $1460^\circ C$, the other at 63 atomic percent SiO_2 with eutectic temperature at $1436^\circ C$.

Three ternary oxide systems have also been chosen for study. The first is $CaO-MgO-SiO_2$, and the second is $BaO-CaO-SiO_2$.⁸ Figures 11 and 12 respectively show their phase diagrams. It can be seen from these phase diagrams that both ternary systems have eutectic points with eutectic temperatures at

Figure 11. A phase diagram of the CaO-MgO-SiO_2 system.

Figure 12. A phase diagram of the BaO-CaO-SiO₂ system.

vicinity of the melting point of silicon. The third is BaO-MgO-SiO₂, which also has an eutectic temperature at the melting point of silicon.

It was not known if the selected mixed oxide systems could fulfill criteria (c) and (d). Experiments were conducted to evaluate these two criteria.

5.2 Experimental Procedure

Reagent grade carbonates were used as oxide sources with the exception of SiO₂.^{*} Two methods were used to add the oxide(s) into the silicon charge. One is to place the powdered oxide(s) on top of the silicon charge. Caution has to be taken to avoid direct contact of the oxide(s) with the quartz crucible. Upon heating the furnace the carbonate(s) decompose before the MG-Si melts. After complete melting of the silicon charge, an inert gas such as Ar was bubbled into the melt for mixing. After mixing a blast of Ar onto the center of the melt surface forces the slag to adhere to the crucible wall. A clean surface was created at the center of the melt and ingot pulling from this melt was possible. Another method of adding the oxide(s) was used. In this case the oxide(s) were pressed into tablets with dimensions of 2 cm dia. by 1.5 cm height. The tablets were carried by a silicon disc which was made from a single crystal seed. The oxide tablets were added to silicon melt and some smoke evolved because of the decomposition of carbonate in the silicon melt. The same procedure as described previously was used to mix the oxide(s) with the silicon melt.

Two types of experiments have been conducted. The first is the study of contamination of silicon by the added oxide(s). Semiconductor grade silicon and a constant amount of boron master alloy were used as dopant in each run. The second is the study of purification of MG-Si by slagging using the added oxide(s).

* The quartz crucible is the source of SiO₂.

Three analytical techniques were used to study the effect of slagging. The emission spectrographic technique was used to analyze the impurities in pulled ingots and slags. Electron microprobe was used to analyze the impurity distribution between the remaining melt and slag phase. The electrical resistivity measurement was used to measure concentration of P-type impurities in pulled ingots.

5.3 Experimental Results

5.3.1 The Contamination Study

The degree of contamination was studied by the change in resistivity of ingots due to the addition of oxide slag. Table XI lists the type and resistivity of ingots. The amount of carbonate(s) used as slagging agent is also given. The results shown in this table can be restated as following:

- (a) CaO-SiO_2 slag does not contaminate Si melts.
The silicon melt remains clean after the addition of this slag. Single crystals can be grown.
- (b) CaO-BaO-SiO_2 slag gives N-type contamination.
Single crystals cannot be grown from the melts.
- (c) BaO-MgO-SiO_2 slag gives P-type contamination.
Single crystals cannot be grown from the melts.
- (d) CaO-MgO-SiO_2 slag does not contaminate Si melt.
Single crystals have not been grown.

5.3.2 Macroscopic Study

An extensive study has been made on the effectiveness of CaO-SiO_2 slag for purification of MG-Si. Table XII shows the impurity concentration in MG-Si melts treated with various amounts of CaCO_3 . The table shows that the aluminum concentration decreases with increase in the amount of CaCO_3 added. Impurities extracted into the CaO-SiO_2 phase after slagging are also shown in this table.

TABLE XI

SLAG CONSTITUENTS, TYPE AND RESISTIVITY OF INGOTS PULLED FROM SLAG TREATED MELTS

<u>SLAG CONSTITUENT</u>	<u>TYPE & RESISTIVITY OF INGOTS</u>	<u>REMARKS</u>
1. None	P, 2.1 Ωcm	Single crystal
2. CaCO_3 , 1% Si	P, 1.99 Ωcm	Single crystal
3. CaCO_3 , 1% Si BaCO_3 , 0.5% Si	P at the seed 2.9 Ωcm N at the tang end 1.9 Ωcm	Poly crystal
4. MgCO_3 , 1% Si BaCO_3 , 1% Si	P, 0.22 Ωcm	Poly crystal
5. MgCO_3 , 15% CaCO_3 , 1%	P, 1.71 Ωcm	Poly crystal

TABLE XII

CONCENTRATION (in PPM wt)* OF IMPURITIES IN SILICON MELTS TREATED BY VARIOUS AMOUNTS OF CaCO_3 .

ELEMENT	Amount of CaCO_3 added in Si melt				CaO-SiO ₂ (1% in Si) After slagging
	0%	0.12%	0.88%	1.0%	
Fe		>1000	>1000	>1000	>1000
Mn		330	330	100	33
Cr		100	100	33	33
Ca		100	33	33	>1000
Sr		1	3	<1	100
Mg		1	<1	<1	100
Ni		100	100	10	10
V		<10	33	10	<10
Ti		330	330	33	330
Cu		33	33	<10	<10
Zr		100	100	10	10
Al	>1000	1000	330	100	>1000
B		<3	<3	<3	<3
Co		10	<10	<10	<10

* measured by emission spectrography

By analysis of this table it can be concluded that CaO-SiO₂ slag has little effect on other impurities, with the exception possible of Al, Sr and Mg.

The measurement of the electrical resistivity of the MG-Si ingots showed that the resistivity increases with the increase in the amount of CaCO₃ added to the melt. Table XIII shows the result. The increase in the ingot resistivity is likely due to the decrease in aluminum concentration.

The effectiveness of using CaO-MgO-SiO₂ slag for MG-Si purification has also been studied. Columns 3 and 4 of Table XIV list the concentration of impurities in the slags after the extraction. There is a high concentration of Fe, Al, and Sr in the slags as compared to that in the original MG-Si. This indicates that CaO-MgO-SiO₂ slag is effective for the removal of these impurities from the MG-Si. The second column of this table lists the impurity concentrations in CaO-SiO₂ slag. It can be seen that the effectiveness of CaO-MgO-SiO₂ slags is only comparable to that of CaO-SiO₂ slags. No advantage is observed by the presence of MgO in the slag phase.

The resistivity of silicon ingots pulled from the melts treated with a CaO-MgO-SiO₂ slag was increased from typically 0.06 Ω cm to 0.09 ~ 0.10 Ω cm range. This also suggests that CaO-MgO-SiO₂ is capable of extracting P-type impurities from MG-Si.

5.3.3 Microscopic Study

The distribution of impurities between the slag and silicon phases was revealed by an electronic microprobe. Figure 13(a) shows a scanning electron micrograph taking across the interface. The right hand side of the micrograph is the CaO-SiO₂ slag phase while the left

TABLE XIII

RESISTIVITY OF SILICON INGOTS
PULLED FROM THE MELTS TREATED
WITH VARIOUS AMOUNTS OF CaCO_3

<u>Amount CaCO_3 (% in Si)</u>	<u>Resistivity (Ω cm)</u>
0.12	0.069
0.88	0.078
1.0	0.082
2.0	0.105

TABLE XIV
 CONCENTRATION OF IMPURITIES IN (PPM wt)
 IN CaO - SiO₂ and CaO-MgO-SiO₂ SLAGS AFTER
 EXTRACTION OF IMPURITIES FROM MOLTEN Mg-Si

<u>Element</u>	<u>2.5% CaCO₃ in Si</u>	<u>5% CaCO₃ .75% MgCO₃</u>	<u>0.5% CaCO₃ 0.2% MgCO₃</u>
Fe	>>1000	>>1000	>>1000
Mn	100	100	10
Cr	33	33	5
Ca	>>1000	>>1000	>>1000
Sr	1000	1000	1000
Mg	1000	>>1000	>>1000
Ni	33	33	<5
V	100	100	10
Ti	100	100	<1
Cu	≤1	≤1	≤1
Zr	100	33	10
Al	>>1000	>>1000	>>1000
B	10	10	10
Co	5	5	5

* measured by emission spectrography

SEM MICROGRAPH 240X
(a)

Fe X-RAY IMAGE
(b)

Ca X-RAY IMAGE
(c)

Al X-RAY IMAGE
(d)

Figure 13. A SEM micrograph (a) and X-ray images radiated from Fe (b), Ca (c) and Al (d).

side is silicon phase. Figure 13(b) through (d) are the X-ray images respectively for Fe, Ca and Al radiation. The density of the bright dots in the micrographs is proportional to the concentration of impurity radiating the X-rays. Figure 13(b) shows that Fe is dispersed throughout the slag phase while it is segregated inhomogeneously in the silicon phase corresponding to the two bright spots in Figure 13(a). EDAX scan of segregated region showed that it contained the following composition of impurities: 11.5% Pt, 1.3% Ca, 16.2% Ti, 5.8% V, 1.8% Mn, and 22.7% Fe.

Figure 13(c) shows that majority of Ca is confined to the slag phase and very little Ca is detected in the silicon phase. Figure 13(d) shows that Al is predominately observed in the slag phase. This confirms the macroscopic observation that CaO-SiO_2 phase is an effective slagging agent for extracting Al from molten MG-Si.

Another example showing the impurity distribution between the slag and silicon phases is illustrated in Figure 14. The slag is made of CaCO_3 (.5% in Si), MgCO_3 (.2% in Si) and SiO_2 which came from the quartz crucible. Again, (a) is a scanning electron micrograph. The upper region is silicon phase while the lower region is the slag phase. The bright spots in the upper region are due to segregation of metallic impurities. The impurities in the "Fe cluster" consisted of .96% Mg, .26% Al, 4.0% Ti, 1.7% V, 0.5% Cr, 1.2% Mn, and 27.5% Fe. The balance is silicon (i.e., 61.7%). Figure 14(b) through (d) are respectively the X-ray images of Ca, Al and Mg radiation. (b) and (d) show that the silicon melt was not contaminated with Ca or Mg by the slag. (c) shows that the slag is also effective for extracting Al from the molten silicon.

SEM MICROGRAPH 240X
(a)

Ca X-RAY IMAGE
(b)

Al X-RAY IMAGE
(c)

Mg X-RAY IMAGE
(d)

Figure 14. A SEM micrograph (a) and X-ray images radiated from Ca (b) Al (c) and Mg (d)

Slags consisting of $\text{CaO} + \text{SiO}_2$ or $\text{MgO} + \text{SiO}_2$ has been found to be effective for the removal of Al and probably a little Sr from molten silicon. They are not effective for removing Fe or other transition metals. It seems that the elements with a high electromotive force can be extracted by an oxide slag, while those with a low electromotive force cannot be extracted. This suggests that the slagging by an oxide requires the oxidation of impurities and then the dissolution of the oxidized impurities into the slag phase. If this hypothesis is correct, it will be rather difficult to find an oxide slag which can oxidize the transition metals. The removal of transition metals requires the use of other techniques. Fortunately the segregation coefficient of the transition metals is generally very low. These impurities can be easily removed by the re-distribution of impurities during freezing or ingot pulling.

6.0 PURIFICATION BY IMPURITY REDISTRIBUTION

6.1 Theoretical Consideration

Purification by impurity redistribution upon ingot pulling perhaps is the most effective method for removing metallic impurities from the MG-Si. Table XV lists the segregation coefficients for various metallic impurities in silicon^{9,10,11,12}. It can be seen that most of the metallic impurities have a segregation coefficient less than 10^{-3} with the exception of aluminum. In other words upon melting and ingot pulling the metallic impurities in the solidified silicon will be approximately three orders of magnitude lower than that in the remaining melt.

More precisely the impurity concentration in the pulled ingot is related to the impurity concentration in the original melt and the segregation coefficient by the following equation:

$$C_s = K C_{ol} (1-g)^{K-1} \quad (3)$$

TABLE XV

SEGREGATION COEFFICIENTS FOR VARIOUS
METALLIC IMPURITIES IN SILICON FOR
DIFFERENT CRYSTAL GROWTH CONDITIONS

Impurity Element	Single Crystal _{ref.}	Polycrystalline _{ref.}	Constitutionally Super Cooled _{ref.}
Al	2.8×10^{-3} to 3×10^{-2}		
Ga	8×10^{-3}		
Bi	7×10^{-4}		
Cu	6.9×10^{-4}	1.7×10^{-2}	0.16
Zn	1×10^{-5}		
Au	2.5×10^{-5}		
Fe	6.4×10^{-6}		
Co	8×10^{-6}		
Te	4×10^{-6}		
Cd	1×10^{-8}		
Mn	1.3×10^{-5}	5.7×10^{-2}	0.429
Mg	3.2×10^{-6}		
Ni	3.2×10^{-5}		
Ti	3.6×10^{-6}		
V	4×10^{-6}		
Zr	$< 1.5 \times 10^{-7}$		
Cr	1.1×10^{-5}		

where: C_s is the impurity concentration in the pulled ingot
 C_{ol} is the impurity concentration in the original melt
 K is the segregation coefficient of the impurity
 g is the fraction of melt pulled

In actual crystal pulling the segregation coefficient is varied with the crystal pulling parameters. Therefore the effective segregation coefficient K_{eff} is used. The effective segregation coefficient is related to the equilibrium segregation coefficient K_0 and the crystal parameters as follows:

$$K_{eff} = \frac{K_0}{K_0 + (1-K_0) \exp \left(\frac{-V\delta}{D} \right)} \quad (4)$$

where: V is the crystal pull rate
 δ is the thickness of boundary layer at the solid-liquid interface
 D is the diffusion coefficient of the impurity at the interface

Equation 4 shows that effective segregation varies with the ingot pull rate. When the ingot pull rate is decreased to zero the effective segregation coefficient approaches the equilibrium segregation coefficient. When the ingot pull rate is increased to infinity, the effective segregation coefficient becomes one. In this case, no purification takes place by ingot pulling. Equation 4 also shows that K_{eff} is affected by the thickness of the boundary layer δ . A smaller value of δ is needed for a smaller K_{eff} value. A high rate of crystal and/or crucible rotation will lead to a decrease in δ .

The effective segregation coefficient also varies with the grain size structure of the ingot being pulled. The effective segregation coefficient is greatly increased when the ingot is pulled from a melt under conditions of constitutional supercooling or when the pulled ingot contains very small grains. Table XV shows the change of segregation coefficient of Cu and Mn under three different crystal pulling conditions. It is therefore important that constitutional supercooling be prevented. The conditions under which constitutional supercooling can be prevented are by:

$$\frac{G}{V} \geq \frac{mC_o(0)(1-K_o)}{K_o D} \quad (5)$$

where: G is the temperature gradient of the melt

V is the crystal pull rate

m is the slope of the binary phase diagram of silicon and impurity of interest

$C_o(0)$ is the impurity concentration in the solid at the solid-liquid interface

K_o is the equilibrium segregation coefficient

D is impurity diffusion coefficient in the melt

Thus in order to prevent constitutional supercooling, the term on the left hand side of equation (5) has to be greater than that on the right hand side of the equation. This can be achieved either by increase in G and/or decrease in ingot pull rate V .

6.2 Experimental Results

As outlined in Section 6.1 impurity redistribution during ingot pulling is perhaps the most effective method of purifying MG-Si melts. Ingot growth runs were carried out in a Hamco 800 crystal puller. Quartz crucibles - 8" wide - were used to contain molten silicon. The melt size used in each experiment was 4 Kg.

Slag was removed from molten silicon either by vacuum treatment or by mechanical means. Ingot growth was always done in an argon ambient even in the case in which slagging was done under vacuum. Three inch ingots were grown with pull rates varying from 1 to 3"/hour. Only first pulled ingots were considered in this study. Wafers were sliced from the seed and tang end of ingots for evaluation.

In order to achieve large grain growth we have used a technique combining a large seed, to initiate growth, together with slow pull rate to delay the onset of constitutional supercooling. We have used a 3" shoulder crystal as the large seed for our experiments. Figure 15 shows a picture of such a shoulder. The shoulder was cut from a dislocation-free (100) crystal. After growth the shoulder can be cut again and reused.

Careful blending of the large seed with the silicon melt is necessary if one wants to avoid the formation of voids in the growing ingot. Figure 16 shows an example of an ingot grown from poor blending of the seed. It shows three consecutive sections cut just below the seed in an ingot grown using a large seed. Void-induced polycrystalline growth is evident.

6.2.1 Impurity Concentration as Function of Distance from the seed.

Early experiments using a large shoulder as a seed had shown that the grain size was greatly increased for a distance of only 1 to 2 inches below the seed. However, the grain size decreased dramatically from there toward the tang end of the ingots. No difference in grain size was observed at the tang end compared to those grown from a smaller diameter (0.38") seed. Figure 17 shows an 8 inch long 3" diameter crystal pulled at a rate of 3.5"/hr using a large seed. Section 1, cut approximately 2 inches below the seed still exhibits large grains bounded by approximately perpendicular

Figure 15. Three inch (100) shoulder used to initiate ingot growth.

Figure 16. Polycrystalline growth induced by poor blending of a large seed with the silicon melt.

Figure 17. MG-Si ingot grown using a 3" (100) shoulder as a seed and relative cross sections.

grain boundaries with the inner portion continuing the (100) seed orientation. Further cuts however show the grain structure considerably deteriorating as shown in sections 2, 3 and 4. The impurity concentration for the four sections and the seed and tang portions of the crystal are listed in Table XVI. The emission spectroscopy data indicate that there is an increase in impurities (especially metals) moving away from the seed (large grains) toward the tang end of the ingot (lamellar structure). A repeated experiment on another ingot showed a similar result. Figure 18 shows the plot of impurity concentration vs the distance from the seed. A dramatic increase in concentration can be seen when the grain structure changes from polygonal to lamellar grains.

6.2.2 Grain Size vs Growth Rate

Figure 19(a) shows 6 wafers cut from a MG-Si ingot grown at a rate of 3"/hr. The wafers were cut from a region extending about 1 inch below the seed and spaced 0.5" in each consecutive cut. A progressive structure deterioration is evident. The effect of slowing the pull rate is manifested in Figure 19(b) which shows 5 wafers cut from MG-Si ingot grown at a rate of 1"/hour. The wafers were cut from similar portions of crystal below the seed as in the first ingot. There is no evidence of constitutional supercooling in Section 5 which is still almost completely single crystal.

Figure 20 compares grain size at the seed and tang ends of 3 MG-ingots. The ingot grown at 3"/hr with a small seed exhibits small polygonal grains at the seed end with a lamellar structure at the tang end (Figure 20,a). The ingot grown at 1"/hr with a small seed has large polygonal grains at the seed and large grains with some lamellae at the tang end (Figure 20,b). Finally the ingot

TABLE XVI

VARIATION OF IMPURITY CONCENTRATION ALONG THE LENGTH OF A MG-SI INGOT.
ANALYSIS BY EMISSION SPECTROSCOPY (PPM W)

<u>Element</u>	<u>MG-187(S)</u>	<u>MG-187(1)</u>	<u>MG-187(2)</u>	<u>MG-187(3)</u>	<u>MG-187(4)</u>	<u>MG-187(T)</u>
Cr	<5	<5	10	10	10	33
Ce	<1	<1	<1	<1	<1	<1
Sr	<5	<5	<5	<5	<5	<5
Mn	<10	<10	33	33	33	100
Al	<5	<5	100	100	100	100
Fe	<2	<2	1000	1000	1000	1000
Ni	<5	<5	10	10	33	33
Co	<5	<5	5	5	5	5
Zr	<10	<10	<10	10	10	<10
Ti	<1	<1	100	100	100	100
Cu	<1	<1	<1	<1	<1	<1
Be	<1	<1	<1	<1	<1	<1
V	<10	<10	33	100	100	100
Mg	<1	<1	33	33	33	10
B	<2	<2	<2	<2	<2	<2
Sn	<5	<5	<5	<5	<5	<5

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Figure 18. Concentration of impurity in a MG-Si ingot as function of distance from the seed.

(a) Growth rate: 3 inches/hour

(b) Growth rate: 1 inch/hour

Figure 19. Comparison of Grain Size as Function of Growth Rate and Distance from the Seed

Figure 20. Comparison of grain size as function of seed size and growth rate at the seed and Tang ends of three MG-Si ingots.

(a) Small seed growth rate: 75 mm/hr. (b) Small seed growth rate: 25 mm/hr.

(c) Large seed growth rate: 25 mm/hr.

grown at 1"/hr utilizing a large seed, is almost single crystal at the seed end and still has large grains at the tang end (Figure 20(c)). Occasionally the lamellar structure was seen at the center region in the tang end of ingots.

6.2.3 Impurity Concentration vs Grain Size

The strong influence exercised by the grain size on the impurity concentration is evident in Table XVII which compares the impurity content (ppmw) analyzed by emission spectroscopy, at the seed and tang end of two of the MG-Si ingots. There is no difference in impurity concentration at the seed and tang end of the large-grained ingot. On the other hand the lamellar section at the tang end of the other ingot contains significant higher impurity content, notably: Fe, Ti, Al, V, Cr and Mn.

Since Table XVII shows that all the impurities in the large-grained ingot are below the resolution limit of the emission spectroscopy technique the same samples were also measured by spark source mass spectrography. Table XVIII shows a complete list of the elements seen in MG-Si ingots by SSMS. The elements not listed in the table are (i) undetectable (O_2 , N, Hg), (ii) present as an instrument source (Ta, Co) or (iii) below 0.1 ppm wt, the resolution limit of the instrument.

6.2.4 Comparison with S.G. Crystals

Comparison by SSMS between two MG-Si ingots and two semiconductor grade (SG) Si crystals is shown on Table XIX. The two SG crystals were P-type, boron doped with resistivity in the range of 0.01 - 0.07 ohm-cm. The MG ingots were also P-type with resistivity in the range of 0.06 to 0.1 ohm-cm. With the exception of Al, P, Ge, B and perhaps Ti the impurity content of the MG ingots is comparable to that of the SG crystals.

TABLE XVII

COMPARISON OF IMPURITY CONCENTRATION, AS A FUNCTION OF GRAIN SIZE AT THE SEED END AND TANG ENDS OF TWO Mg-Si INGOTS. (PPM wt)

Element	Large Grains MG-185(S)	Lamellar MG-185(T)	Large Grains MG-196(S)	Large Grains MG-196(T)
Cr	<5	100	<5	<5
Ca	<1	3.3	<1	<1
Sr	<5	<5	<5	<5
Mn	<1	100	<1	<1
Al	<5	330	<5	<5
Fe	<2	>1000	<5	<5
Ni	<5	33	<5	<5
Co	<5	10	<5	<5
Zr	<10	10	<10	<10
Ti	<1	330	<1	<1
Cu	<1	3.3	<1	<1
Be	<1	<1	<1	<1
V	<5	100	<10	<10
Mg	<1	10	<1	<1
B	<10	<10	<10	<10
Sn	<5	<5	<5	<5

TABLE XVIII

COMPARISON OF IMPURITY CONCENTRATION, AS A FUNCTION OF GRAIN SIZE
AT THE SEED AND TANG ENDS OF TWO MG-Si INGOTS. ANALYSIS
BY S.S. MASS SPECTROGRAPHY. (PPM WT)

Element	Large Grains MG-185(S)	Lamellar MG185(T)	Large Grains MG-196(S)	Large Grains MG-196(T)	Element
W	<0.11	0.12	< 0.11	<0.11	W
Gd	<0.11	1.1	<0.11	<0.11	Gd
Cd	<0.15	0.44	0.34	<0.15	Cd
Mo	0.10	0.96	< 0.11	<0.11	Mo
Ge	0.10	0.48	0.72	0.72	Ge
Cu	0.02	0.50	0.02	0.03	Cu
Ni	0.45	19	0.65	0.53	Ni
Fe	0.13	840	0.14	0.30	Fe
Mn	0.04	370	0.07	0.19	Mn
Cr	--	57	--	--	Cr
V	--	91	--	--	V
Ti	0.08	210	0.03	0.32	Ti
Ca	--	9.8	--	0.37	Ca
Cl	2.3	1.6	0.24	0.27	Cl
S	3.0	--	0.12	0.20	S
P	3.7	3.7	1.4	1.8	P
Al	60	3300	60	47	Al
Mg	0.15	36	--	0.11	Mg
Na	0.20	< 0.55	--	0.27	Na
C	12	28	3.4	3.4	C
B	0.42	0.73	0.28	0.28	B

TABLE XIX

COMPARISON OF IMPURITY CONCENTRATION AT THE SEED AND TANG ENDS OF TWO LARGE
GRAINED MG-Si INGOTS WITH SG CRYSTALS
ANALYSIS BY S.S. MASS SPECTROGRAPHY (PPMW)

Element	MG-195(S)	MG-195(T)	MG-196(S)	MG-196(T)	T36R07*	L-62**	Element
W	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	W
Gd	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	Gd
Cd	<0.15	<0.15	0.34	<0.15	<0.15	<0.15	Cd
Mo	0.12	0.13	<0.11	<0.11	<0.11	0.16	Mo
Ge	0.24	0.36	0.72	<0.72	--	--	Ge
Cu	0.02	0.02	0.02	0.03	0.01	0.01	Cu
Ni	<0.29	0.32	0.65	0.53	--	0.39	Ni
Fe	0.16	<0.09	0.14	0.30	0.10	0.10	Fe
Mn	<0.05	0.07	0.07	0.19	0.07	0.07	Mn
Ti	0.15	0.23	0.03	0.32	0.08	0.03	Ti
Ca	--	--	--	0.37	0.42	--	Ca
K	--	--	--	0.50	--	--	K
Cl	2.1	2.4	0.24	0.27	0.24	0.18	Cl
S	0.40	0.60	0.12	0.20	0.20	0.17	S
P	0.65	1.1	1.4	1.8	0.37	0.28	P
Al	82	39	60	47	0.16	0.07	Al
Mg	0.16	--	--	0.11	--	--	Mg
Na	--	--	--	0.27	0.10	--	Na
F	--	0.10	--	--	0.17	--	F
C	6.0	4.0	3.4	3.4	1.6	3.4	C
B	0.55	0.28	0.28	0.04	0.04	0.66	B

* 0.04 - 0.07 Ω cm, P-type (Boron)

** 0.01 - 0.03 Ω cm, P-type (Boron)

7. ASSESSMENT OF PURIFICATION TECHNIQUES

The relative value of the five purification techniques discussed in this report is summarized on Table XX.

Of the four purification steps performed in the crystal puller by far the most effective is the crystal growth process itself if constitutional supercooling of the melt can be avoided. If this is the case MG-Si ingots can be grown on the first pull which contain impurity levels at the vicinity of the detection limit of SSMS with the exception of Al, Ti, Ge, P and B. We feel that both the reactive gas treatment and the slagging (liquid-liquid extraction) steps can be omitted without effecting the final purity achieved. This leaves the phase separation step either by physical means or by vacuum as the only essential step to be performed in the crystal puller prior to ingot growth.

Acid leaching by hot aqua regia was found effective in removing Al from pulverized MG-Si. It is however a tedious, involved process and could present serious environmental waste disposal problems if done on a large scale.

8. SOLAR CELL FABRICATION

8.1 Epitaxial Deposition

Since an epitaxial layer thickness of 15 μm was considered adequate by previous investigators¹³, this thickness was arbitrarily chosen to build the first solar cells. Only high purity large-grained substrates were used having a resistivity of 0.06 $\Omega\text{-cm}$. The wafers were texturized in a anisotropic KOH/IPA solution prior to epi. However, the epitaxial layer tended to obliterate the peaks. The epi layers were deposited via the hydrogen reduction of SiHCl_3 in a vertical reactor at a temperature of 1150°C. They were P-type doped with B_2H_6 to a doping level of 2×10^{16} atoms/cm³. Actual epi thickness was approximately 17 μm .

TABLE XX

ASSESSMENT OF PURIFICATION TECHNIQUES

<u>PURIFICATION TECH.</u>	<u>IMPURITY REMOVAL</u>	<u>REMARKS</u>
Acid leaching	Most metals, very slow rates	Environmental problems with waste disposal
Phase separation	Insoluble Al, Ca, Mg	Essential for ingot pulling
Physical Vacuum		
Reactive gas	Some metals not consistent	Can be omitted
Slagging (extraction)	Al, Sr, Mg	Crucible can't be reused
Impurity Redistribution	Most "Elements" except Al, Ge, Ti, P, B	Most effective

Figure 21 shows the spreading resistance profiles of the epi layers deposited on a grain of (100) orientation and on a grain of (221) orientation on MG-Si substrates. As a comparison the profile on a SG-Si substrate is also shown.

8.2 Solar Cell Process

The solar cell process used in making the first batch of solar cells consisted of the following main steps:

- (1) N^+ Diffusion
- (2) AR Coating
- (3) Silver Screen Front Metal Contact
- (4) Sinter
- (5) Silver Screen Back Metal Contact
- (6) Sinter
- (7) Plasma Etch Edges

N^+ diffusion is done @ 900°C using PH_3 as a source. Typical diffusion depth from 0.4 to 0.5 μm are obtained. The AR coating consisted of $\sim 750 \text{ nm}$ of vacuum deposited Si_3N_4 . The metallization is a Motorola proprietary process utilizing silver-screened technology and the Al back field. Following metallization the wafers are plasma-etched to remove the junction from the edge. Together with the MG-Si wafers we have also run SG wafers (no epi) for control.

8.3 Solar Cell Electrical Characteristics

The electrical characteristics for 3" MG-Si epitaxial solar cells are summarized on Table XXI. Average sheet resistance in the N^+ diffused layer for the MG-Si wafers is $31.7 \Omega/\square$, while that of the control wafers is $29.75 \Omega/\square$. This can be interpreted as due to compensation occurring during PH_3 diffusion. There was also some peeling of the front metal contact which may account for some low readings. Shadowing effects in the electrical test station also resulted in values for the FF about 6% lower than that using a curve tracer.

Figure 21. Spreading resistance plot of the epi profiles for a SG and a MG-Si substrate.

TABLE XXI

EPITAXIAL SOLAR CELL ELECTRICAL CHARACTERISTICS

<u>CRYSTAL</u>	<u>NO.</u>	<u>R sq.</u>	<u>FF</u>	<u>Voc</u>	<u>Isc</u>	<u>η(%)</u>
P06 *	1	26.6	0.74	0.600	1.495	14.6
MG-195	2	32.1	0.58	0.505	1.000	6.4
MG-195	3	30.2	0.59	0.525	1.005	6.8
MG-195	4	31.6	0.55	0.510	1.030	6.3
MG-195	5	31.6	0.58	0.515	1.010	6.6
P06	6	28.9	0.60	0.600	1.515	12.0
MG-195	7	31.0	0.55	0.510	1.050	6.5
MG-195	8	31.9	0.58	0.490	0.010	6.3
MG-195	9	31.5	0.52	0.495	0.995	5.6
MG-195	10	31.3	METAL PEELED			
P06	11	30.2	0.69	0.600	1.495	13.6
MG-195	12	31.0	0.61	0.530	0.990	7.0
MG-195	13	32.7	0.57	0.490	1.015	6.2
MG-195	14	33.8	0.53	0.510	1.070	6.3
P06	15	33.3	0.65	0.600	1.525	13.1

* control

The IV characteristics of a solar cell fabricated on a epitaxial layer utilizing a MG-Si substrate are given in Figure 22. As comparison a control cell fabricated on a SG substrate is also shown. Generation currents under AM1 condition as well as the dark currents for both cells are shown. The main electrical parameter limiting cell performance seems to be the short circuit current which is approximately 30% less than that of the control cell. These results are similar to those reported in the literature¹⁴, for epitaxial solar cell utilizing polycrystalline MG-Si substrates.

The IV characteristics of the MG-Si solar cell in both the forward dark and the illuminated generation curves appear very similar to the control cell. The voltage loss due to series-contact resistance in the MG-Si cell is 20 mV while the loss in the control cell is 39 mV. Dividing by the respective short circuit current this gives a series resistance of 0.21Ω in the MG-Si cell and 0.27Ω in the control cell. There does appear to be a very slight softening of the IV curve for the MG-Si cell indicating a possible higher recombination in the junction area (lower lifetime) than the control cell. Another cause of the lower performance in the MG-Si cell may also be the thickness of the cell active region which gives the photons only a limited thickness of high lifetime material in which to create carriers. Only a small number of the photons create carriers in the thin epi layer, and most of the carriers produced in the MG-Si substrate are consumed by recombination. The MG-Si cell therefore appears much like a standard Cz cell under a lower illumination. Further experiments with varying active layer thickness should verify this effect.* Further reduction in the concentration of lifetime killer impurities such as Ti should help the increase in minority carrier lifetime. The improvement of defect density and control of the out-diffusion of impurities from the substrate may reduce the recombination current.

* The follow-up experiments using a 50 μ m thick epitaxial layer have produced solar cells with an efficiency greater than 10%.

Figure 22. Illuminated and dark forward IV characteristics of a solar cell fabricated on a MG-Si substrate and of a cell fabricated on a SG substrate.

9. FUTURE WORK

The following lists the specific items of work to be conducted in the second year of the program:

- (1) Optimization of purification and ingot formation processes.
The goal of this work is to produce polycrystalline silicon with a cost of less than \$10/kg. The produced polycrystalline silicon will contain (1) metallic impurities less than 10 ppm each, and 2) grain size of 3mm x 3 mm or larger.
- (2) Growth of epitaxial silicon layer by three different techniques:
 - (a) one atmosphere chemical vapor deposition
 - (b) low pressure chemical vapor deposition
 - (c) the laser regrowth technique
- (3) Fabrication and evaluation of solar cells built on the epitaxial grown by the aforementioned techniques and on substrates without epitaxial layer.
- (4) Preparation of double-pull ingots and investigation of the improvement of the ingot quality by this additional ingot pulling.
- (5) Correlation of solar cell efficiency with the variables in substrate quality and the methods of epitaxial Si growth.
- (6) Economic analysis of substrate and epitaxial growth process and recommendation of the promising processes.

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