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

Quarterly Technical Progress Report No. 2 for January 1—March 31, 1980

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May 1980

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Motorola, Inc.
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U.S. Department of Energy

Solar Energy

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FOR THE
PRODUCTION OF LOW COST SILICON SUBSTRATES

QUARTERLY TECHNICAL PROGRESS REPORT NO. 2
FOR PERIOD
1 JANUARY 1980 - 31 MARCH 1980

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MAY 1980

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UNDER DOE SUBCONTRACT NO. XS-9-8119-3

MOTOROLA PROJECT NO. 2376

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I. 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. This is because of the following reasons: (1) It contains 1 to 2% metallic impurities. The metallic impurities are regarded as minority carrier lifetime killers. Furthermore, even the MG-Si is used as substrates for the thin film solar cells, the high diffusivity of the metals 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 are 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 become single crystals or large grain polycrystalline form for electronic device or solar cell applications.

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 are performed in a consecutive manner using a crystal puller with the exception of step (1). The purified ingots will be in a desired ingot dimension and further recrystallization is not necessary.

In this quarterly period we have completed the study of the purification by (1) reactive gas treatment, and 2) slagging. Selection of reusable crucible has also been made.

II. THEORETICAL CONSIDERATION

1. Purification by Reactive Gas Treatment

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 of 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.

1.1 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 the 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.

1.2 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.

1.3 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.

1.4 The volatility of compounds

The volatility of reaction compounds has been surveyed. Table I 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 gases and metal impurities may probably escape from the silicon melt.

TABLE I

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

2. Purification by Slagging

The 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 at a temperature 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 seems 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 1 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°C , the other at 63 atomic percent SiO_2 with eutectic temperature of 1436°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 . Figures 2 and 3 respectively show their phase diagrams². It can be seen from these phase diagrams that both ternary systems have eutectic points with eutectic temperatures at vicinity of the melting point of silicon. The third is BaO-MgO-SiO_2 , which also has an eutectic temperature by the melting point of silicon.

It was not known if the selected mixed oxide systems could fulfill criteria (3) and (4). Experimental work was needed. The experimental results are to be presented in this quarterly progress report.

A PHASE DIAGRAM OF THE CaO-SiO_2 SYSTEM

Figure 1

A PHASE DIAGRAM OF THE CaO-MgO-SiO_2 SYSTEM

Figure 2

A PHASE DIAGRAM OF THE BaO-CaO-SiO₂ SYSTEM

Figure 3

III. EXPERIMENTALS

1. Reactive Gas Treatment

1.1 Procedure

The reactive gases, HCl and SiF₄ have been used for treatment of molten silicon. The arrangement of apparatus was shown in the previous quarterly technical report. Electronic grade HCl and reagent grade SiF₄ were used. Each reactive gas was diluted with He or Ar prior to bubbling into silicon melt. In each experimental 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 SiF₄ 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 was removed by a physical means as described in the previous technical report. 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 solified 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.

1.2 Experimental Results

Table 2 summarizes the analytical results for the ingots pulled from the melts treated with 0, 1.5 l, 4.5 l and 7.08 l HCl. The numbers without parentheses are the concentrations analyzed by emission spectroscopy, while those with parentheses are the concentration analyzed by spark source mass spectroscopy. At the seed end of the ingots the analytical results obtained by the emission spectrography 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 spectrography (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 in Cu concentration.

The concentration of impurities in the melts remaining in the quartz crucible is shown in Table 3. 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 7.08l HCl.

TABLE 2

COMPARISON OF IMPURITY CONCENTRATION (PPM wt) IN SILICON
INGOTS FROM THE MELTS TREATED WITH VARIOUS AMOUNTS OF CH₁.

Element	No HCl	SEED END OF INGOTS (Polygonal structure)		No HCl	TANG END OF INGOTS (lamellar structure)			
		1.5L HCl	4.5L 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

TABLE 3

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
A	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 4 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 3) the concentration of Cr, Ca, Mn and Ti was lower in the treated sample by a factor of 3.

1.3 Discussions

In the patent literature³, it has been claimed that the 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 metallic impurities were reduced by approximately a factor of 3 in concentration. The present work using HCl or SiF_4 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 AlF_3 .

2. Purification by Slagging

2.1 Experimental Procedures

The reagent grade of carbonates were used as oxide sources with the exception of SiO_2 . The quartz crucible containing molten silicon by itself is the source of SiO_2 . Two methods were used to add the oxide(s) into silicon charge. The one is to place the powder of oxide(s) on the top of silicon charge.

TABLE 4

IMPURITY CONCENTRATION (PPM wt) IN THE SILICON
INGOT PULLED FROM A SiF_4 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

Caution has to be taken to avoid the direct contact of the oxide(s) with quartz crucible. Upon heating of the furnace the carbonate(s) decompose before the melting of MG-Si. After the complete melting of the silicon charge, an inert gas such as Ar was bubbled into the melt for mixing. After mixing a proper blast of Ar onto the center of the melt surface it forced 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 the dimension 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 constant amount of boron master alloy were used in each run. The second is the study of purification by slagging using the added oxide(s).

Three analytical techniques were used to study the effect of slagging. The emission spectrophotographic 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.

2.2 Experimental Results

2.2.1 The Contamination Study

The degree of contamination was studied by the change in resistivity of ingots due to the addition of oxide slag. Table 5 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.

2.2.2 Purification Study

2.2.2.1 Macroscopic Study

An extensive study has been made on effectiveness of CaO-SiO_2 slag for purification of MG-Si. Table 6 shows the impurity concentration in MG-Si melts treated with various amounts of CaCO_3 . The table shows that the aluminum concentration decreases with the increase in the amount of CaCO_3 added. The comparison of CaO-SiO_2 after slagging is also shown in this table. By analysis of this table it can be concluded that CaO-SiO_2 slag has little effect on other impurities possibly with the exception of Al and Si.

TABLE 5

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 6

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

The measurement of the electrical resistivity of the ingots showed that the resistivity increases with the increase in the amount of CaCO_3 added to the melt. Table 7 shows the result. The increase in the ingot resistivity is likely due to the decrease in aluminum concentration.

The effectiveness of using CaO-MgO-SiO_2 slag for purification has also been studied. Columns 3 and 4 of Table 8 list the concentration of impurities in the slags after the extraction of impurities. Note that a high concentration of Fe, Al and Sr in the slags was seen. For comparison with CaO-SiO_2 slag, the first column of this table lists its impurities concentration. It can be seen that the effectiveness of CaO-MgO-SiO_2 slags are comparable to that of CaO-MgO slags.

The resistivity of silicon ingots pulled from the melts treated with a CaO-MgO-SiO_2 slag was increased from typically $0.06 \, \Omega\text{cm}$ to $0.09 \sim 0.10 \, \Omega\text{cm}$ range. This also suggests that CaO-MgO-SiO_2 is capable of extracting P-type impurities from Mg-Si.

2.2.2.2 Microscopic Study

The distribution of impurities between the slag and silicon phases were revealed by an electron microprobe. Figure 4 (a) shows a scanning electron micrograph taking across the interface. The right hand side of the micrograph is the slag phase while the left side is silicon phase. Figure 4 (b) through (d)

TABLE 7

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

<u>Amount CaCO_3</u> <u>(% Si)</u>	<u>Resistivity</u> <u>(Ω cm)</u>
0.12	0.069
0.88	0.078
1.0	0.082
2:0	0.105

TABLE 8

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

Element	2.5% CaCO ₃ in Si	5% CaCO ₃ .75% MgCO ₃	0.5% CaCO ₃ 0.2% MgCO ₃
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

A SEM MICROGRAPH (a) and X-RAY IMAGES
RADIATED FROM Fe (b), Ca (c) and Al (d).

SEM MICROGRAPH 240X
(a)

Fe X-RAY IMAGE
(b)

Ca X-RAY IMAGE
(c)

Al X-RAY IMAGE
(d)

Figure 4

are the X-ray images respectively for Fe, Ca and Al radiation. The density of the bright dots in the micrographs are proportional to the concentration of impurity radiating the X-rays. Figure 4 - (b) shows that Fe is dispersed throughout the slag phase while it is segregated inhomogeneously in the silicon phase correspond to the two bright spots of high density X-ray radiation from Fe impurity in Figure 4-(b). EDAX scan of a 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% V, 1.8% Mn, and 22.7% Fe.

Figure 4 - (c) shows that majority of Ca is confined to the slag phase and very little Ca is detected in the silicon phase. Figure 4 - (d) shows that Al is predominately observed in the slag phase. This confirms the macroscopic study 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 5. The slag is made of CaCO_3 (.5% Si), MgCO_3 (.2% Si) and SiO_2 which came from 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 the segregation of metallic impurities. The impurities in the area (a) consisted of .96% Mg, 2.6% Al, 4.0% Ti, 1.7% V, 0.5% Cr, 1.2% Mn, and 2.75% Fe. The balance is silicon (i.e., 61.7%). Figure 5 - (b)

A SEM MICROGRAPH (a) AND X-RAY IMAGES
RADIATED FROM Ca (b), Al (c) and Mg (d)

SEM MICROGRAPH 240X
(a)

Ca X-RAY IMAGE
(b)

Al X-RAY IMAGE
(c)

Mg X-RAY IMAGE
(d)

Figure 5

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.

2.3 Discussions

The slag consisted of $\text{CaO} + \text{SiO}_2$ or $\text{CaO} + \text{MgO} + \text{SiO}_2$ has been found to be effective for the removal of Al and probably a little Sr from molten silicon. It is 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.

3. Crucible Selection

3.1 Material CONSIDERATION

Currently quartz is the only crucible material which is used in Czochralski furnaces for silicon crystal growth. Quartz crucibles crack upon freezing of silicon melts which remain in the crucibles. Quartz crucibles cannot be reused and contribute to a significant portion of the total growth cost.

The purpose of this task is to select one type of crucibles which can be repeatedly used.

Molten silicon has been considered as a universal solvent. Almost every metal can form an alloy with molten silicon. Therefore, metal crucibles have been excluded for consideration. The ceramic materials are more inert to molten silicon. However, they are relatively porous and can possibly be leached through by the silicon melt.

Crucibles made of high density graphite, such as Pogo graphite and vitreous carbon have been used for polycrystalline silicon ribbon growth. Large size crucibles are not available commercially. In addition high cost of either of these two materials has been excluded for consideration for use in a low cost process.

Survey on physical properties of various grades of commercially available graphite has been made. Ultra carbon's UT-86 has been selected. It appears that UT-86 exhibits high density (1.8), fine grain (.0007 in.), low porosity (19%) and uniform structure. Special orders were made to fabricate crucibles out of this material.

3.2 Experimental Procedures

A 6" diameter and 6" high UT-86 graphite crucible was used in a NRC crystal puller. The experiments were performed for two purposes: One to determine if there is any contamination of the silicon melt from a UT-86 graphite crucible. The other is to test the re-usability of the crucible. For the contamination test, non-doped semiconductor grade silicon charge was used. The degree of the contamination was evaluated

from (1) resistivity values of the pulled ingots, and
2) carbon concentration in silicon crystals. The carbon concentration was measured by the infrared absorption at $16\ \mu$.

3.3 Experimental Results

Effort was not made to select a graphite with the same thermal expansion coefficient as silicon. There may be some mechanical stress to the graphite crucible if the frozen silicon remains in the crucible. However, effort was made to pull all the molten silicon out of the crucible. It has been found out that this is rather easy to accomplish since molten silicon does not wet graphite. When the silicon melt was pulled to dry, a minimum amount of impurities remains in the crucible. Figure 6 shows a top view of used graphite crucible. The roughness on the bottom of the crucible is due to a thin layer of silicon.

The electrical resistivity of pulled ingots is over $115\ \Omega\text{cm}$. This suggests that silicon was hardly contaminated by the doping impurities. The concentration of carbon was in the range of $5\text{ to }6 \times 10^{17}$ atoms/cc, which is the saturation concentration.

3.4 Discussions

The experiments of UT-86 graphite crucible for the semiconductor grade melts look very encouraging. There is no reason to believe that this crucible cannot be repeatedly used for MG-Si melts. It has been planned that a 8" diameter crucible will be used in the next quarter for the MG-Si melts.

TOP VIEW OF A USED GRAPHITE CRUCIBLE

Figure 6

IV. PLANS FOR THE NEXT QUARTER

In the next quarter we plan to perform:

- (a) Purification by vacuum treatment.
- (b) Growth of large grain silicon ingots.
- (c) Epitaxial deposition of silicon on the low cost polycrystalline silicon substrates.
- (d) Continue on the materials evaluation.

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