DOE/JPL-954559-78/1
Distribution Category UC-63

# Solar Silicon via the Dow Corning Process

(NASA-CR-157065) SOLAR SILICON VIA THE DOW CORNING PROCESS Quarterly Report (Dow Corning Corp.) 17 p HC A09/MF A01 CSCL 10A

N78-24637

Unclas
G3/44 20691

QUARTERLY REPORT NO. 6

January 1978

L. P. HUNT, V. D. DOSAJ
and J. R. McCORMICK
DOW CORNING CORPORATION
Solid-State Research and Development Laboratory
Hemlock, Michigan 48626

JPL Contract NO. 954559

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Department of Energy, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of lowcost solar arrays.



DOW CORNING

DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640

DOE/JPL-954559-78/1
Distribution Category UC-63

# Solar Silicon via the Dow Corning Process

QUARTERLY REPORT NO. 6

January 1978

L. P. HUNT, V. D. DOSAJ
and J. R. McCORMICK

DOW CORNING CORPORATION
Solid-State Research and Development Laboratory
Hemlock, Michigan 48626

JPL Contract NO. 954559

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Cor'tract NAS7-100 for the U.S. Department of Energy, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the developm9nt of lowcost solar arrays.

DOW CORNING

DOW CORNING CORPORATION, MIDLAND, MICHIGAN 48640

ABSTRACT

Quartz, as the silicon source material, has been identified to be plentifully available at a sufficient purity and reactivity to meet the objective of this program. Further investigations of deposits are warranted when the program reaches a higher level of development.

Carbon, as a reductant for quartz, must be made available so as to have suitable reactivity in conjunction with high purity, especially with respect to boron and phosphorus. A detailed experimental plan has been developed to do this. Different sources of carbon have been selected to be subjected to various purification methods and reactivity-enhancement processes.

A developmental-scale arc furnace has been installed and will undergo start-up during January. This equipment will be ready next quarter to perform quartz-carbon reactivity testing.

An updated economic analysis of the Dow Corning Process for SoG-Si shows the manufacturing cost to be $7.37/kg (January 1975 dollars) at a level of 2700 metric tons per year. The capital investment would be $38.2 million.

CONTENTS

## I. INTRODUCTION

This contract began on July 31, 1976. This sixth quarterly report covers activities performed during the three months of October, November, and December, 1977.

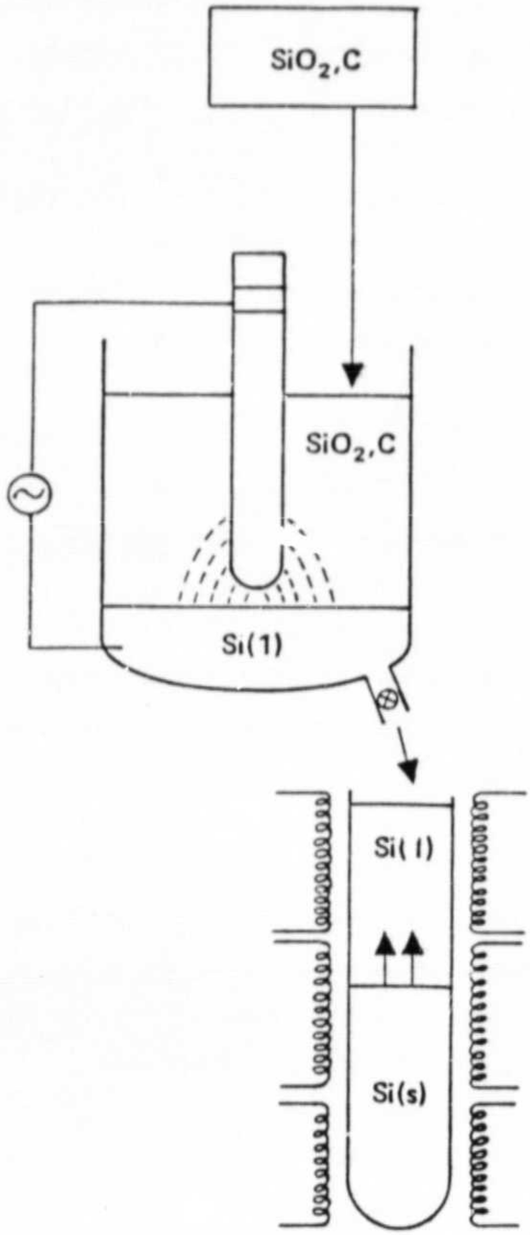
The objective of this program is to demonstrate the feasibility of a process for the production of solar-cell-grade silicon. This process should have high probability of producing silicon for sale at less than \$10/kg when scaled to 3000 metric tons per year by, or before, 1986.

The program tasks involved in the Dow Corning Process for producing solar-grade silicon (SoG-Si) are diagramatically presented in Fig. 1. Task A involves obtaining high-purity raw materials in order to minimize the introduction of impurities into the silicon production step. An extensive survey of quartz and quartzite sources has indicated that large quantities of these materials are available at reasonable cost and with sufficient purity (1).

Charcoal, commercially used as a reductant for quartz in Brazil, has been shown to be of higher purity in most trace elements than commercial reductants commonly used today in the USA (2). It was further demonstrated that charcoal can be purified at high temperature to reduce impurity levels below the detection limits of emission spectroscopy, i.e., about 10 ppmw (2).

Task B is concerned with the reaction of high-purity raw materials to produce high-quality silicon. This is being accomplished through optimization of the $SiO_2$ reduction process. The feasibility of smelting high-purity quart· with commercial charcoal has been established (2). The produced silicon was purer than MG-Si by about an order of magnitude for all analyzed elements. Most silicon produced to date from both high-purity quartz and charcoal has been sufficiently pure to be a good material for final purification in Task C. Difficulties have been incurred, however, in reacting quartz with purified charcoal.

Task C involves final purification via unidirectional solidification using either a Czochralski or Bridgman-type technique to effectively segregate most impurities from the solid into the melt. It is this unidirectionally solidified material that would be supplied to the Large




PROGRAM TASKS

A. Quartz and Carbon Raw Materials

B. Silicon Production via the Reaction $SiO_2 + 2C \rightarrow Si + 2CO$

C. Unidirectional Solidification of Silicon

Figure 1. Schematic Diagram of the Dow Corning Process for Producing SoG-Si

Area Silicon Sheet Task. Purification via the Bridgman-type process has been demonstrated (4); further studies are required to determine the effects of solidification method and rate on purification effectiveness and cost. The Czochralski process has been used to purify silicon produced in Task B. A polycrystalline ingot pulled from such material was analyzed to have transition metal impurities below their limits of detection of approximately 1 ppba or less (5), essentially equivalent to the concentrations in semiconductbr-grade silicon. The best silicon to date has contained 9 ppma boron and 12 ppma phosphorus. These levels must be further reduced through efforts in Tasks A and B.

SoG-Si from Task C was evaluated as solar cells using in-house efforts. Single-crystal material (ca. 60-% yield) was produced by float-zoning a Czochralski pulled ingot which was supplied to Spectrolab for fabrication into cells. Conversion efficiencies at AMO averaged 11 %. Standard cells processed at the same time showed 13 % efficiencies. Further improvements are anticipated when boron levels are reduced through efforts in Task A.

A cost analysis of the Dow Corning Process indicated that the SoG-Si should cost (no profit) close to $7/kg (January, 1975 dollars) to produce at a level of about 3000 Mt/y (4).

The next section of this report details the goals, experimental approach, and progress to date in the various task areas.

## II. TECHNICAL DISCUSSION

### A. Task A - Raw Materials

#### 1. Quartz

Various sources of domestic and foreign quartz have been shown to be available to meet the objective of the Dow Corning Process for producing SoG-Si (3). More detailed work will be performed in evaluating these sources after other tasks of this program have proceeded further.

#### 2. Carbon

Standard graphite electrodes have been fluorocarbon treated at 2500 °C to a sufficient level of purity without altering the electrical characteristics of the electrodes (3).

The main carbon reductant used in the experimental arc furnace produced SoG-Si with metal concentrations in the part-per-billion range or less (4). However, boron and phosphorus levels must be further reduced in the carbon raw material since they are not as effectively removed as metals during processing. Table 1 shows the fractional removal of boron and phosphorus during the silicon production and unidirectional solidification steps.

Table 1. Impurity Removal During Processing

| Impurity | Process (Fractional Reduction) | | |
|---|---|---|---|
| | Silicon Production | Unidirectional Solidification | Overall |
| B | 0.66 | 0.8 | 0.5 |
| P | 0.14 | 0.6 | 0.08 |

It is known that a boron concentration of about 2 ppma (0.3 ohm-cm) results in a maximum in solar cell efficiency (4). Progress in reaching this goal has been quite good in that the level of 9 ppma (0.1 ohm-cm) boron has already been attained (4).

The situation for phosphorus is not as clear cut. Recent results have indicated that considerable phosphorus compensation can exist without serious reduction in solar-cell efficiency. For example, solar cells fabricated from silicon containing 11 ppma boron and 6 ppma phosphorus gave efficiencies 90 % of baseline material (4). Recent information from the Westinghouse-Dow Corning solar-grade silicon definition program has shown that cells fabricated from 0.4 ohm-cm silicon (1 ppma B) that was 80 % compensated (0.8 ppma P) showed an efficiency that was the same as the baseline standard.

Based on the data above, the intermediate goal for the concentration of phosphorus is 1 ppma for this program. It may be necessary to modify this goal somewhat based on future results from the SoG-Si definition programs.

An expanded effort is being planned for obtaining a form of carbon that is sufficiently pure as well as reactive enough for use in the silicon production step. A survey of potential carbon materials has been made and those most probable to meet purity/reactivity goals have been selected. Various purification techniques have been chosen for applying to the selected carbon materials. Several methods have also been determined for modifying the physical structure of the carbon materials in order to increase their reactivity. An initial program plan was developed and awaits approval by JPL.

B. Task B - Silicon Production

A Dow Corning-purchased, 200-kVA arc furnace arrived on site and was installed in a building that had been modified for this type of operation. A Dow Corning-purchased baghouse for silica dust recovery was interfaced with the furnace and auxiliary equipment. Standard operating procedures were written in preparation for a pre-start-up safety inspection.

Furnace start-up is anticipated for late January. Shake-down and baseline experiments will follow in February with close interface with the Raw Materials Task in order to evaluate carbon materials under consideration.

## C. Task C - Unidirectional Solidification

No significant effort was spent on this task during the quarter in anticipation of a Unilateral Modification from JPL.

## III. COST ANALYSIS

An economic analysis was presented based upon the outline of the Dow Corning process, shown in Fig. 2., for producing SoG-Si. Details concerning the assumptions made in this analysis are detailed in a previous quarterly report (4). The basic silicon production process is built around a 3000-Mt/y commercial process that operates at a yield of about 80 %. Since the unidirectional solidification step is assumed to have a 90-% ingot yield, its output is 2700 Mt/y of SoG-Si.

The cost analysis for Dow-Corning-Process Silicon has been updated to

- report costs in January 1975 dollars, rather than October 1977 dollars as done previously;
- correct arithemtic errors;
- use a more realistic depreciation rate of 7 years for crystal-growth equipment, rather than 14 years as done previously.

Two cost analyses are presented below - one for the silicon production process and the other for the final solar-cell-grade silicon. This latter process uses the pure arc-furnace silicon as a raw material to an ingot-growth, purification process using Czochralski technology.

A summary of the costs for producing SoG-Si via the Dow Corning Process are shown in Table 2. The costs in October 1977 dollars have been converted to January 1975 dollars by making the simplifying assumption of an 8-% constant inflation rate over the 2.75-year period ($1.08^{2.75}$ = 1.236).

Table 2. Manufacturing Costs for Dow-Corning-Process Silicon in 1975 and 1977 Dollars

| Date | Manufacturing Costs | |
|---|---|---|
| | Operating ($/kg) | Capital ($M) |
| January 1975 | 7.37 | 38.2 |
| October 1977 | 9.11 | 47.2 |

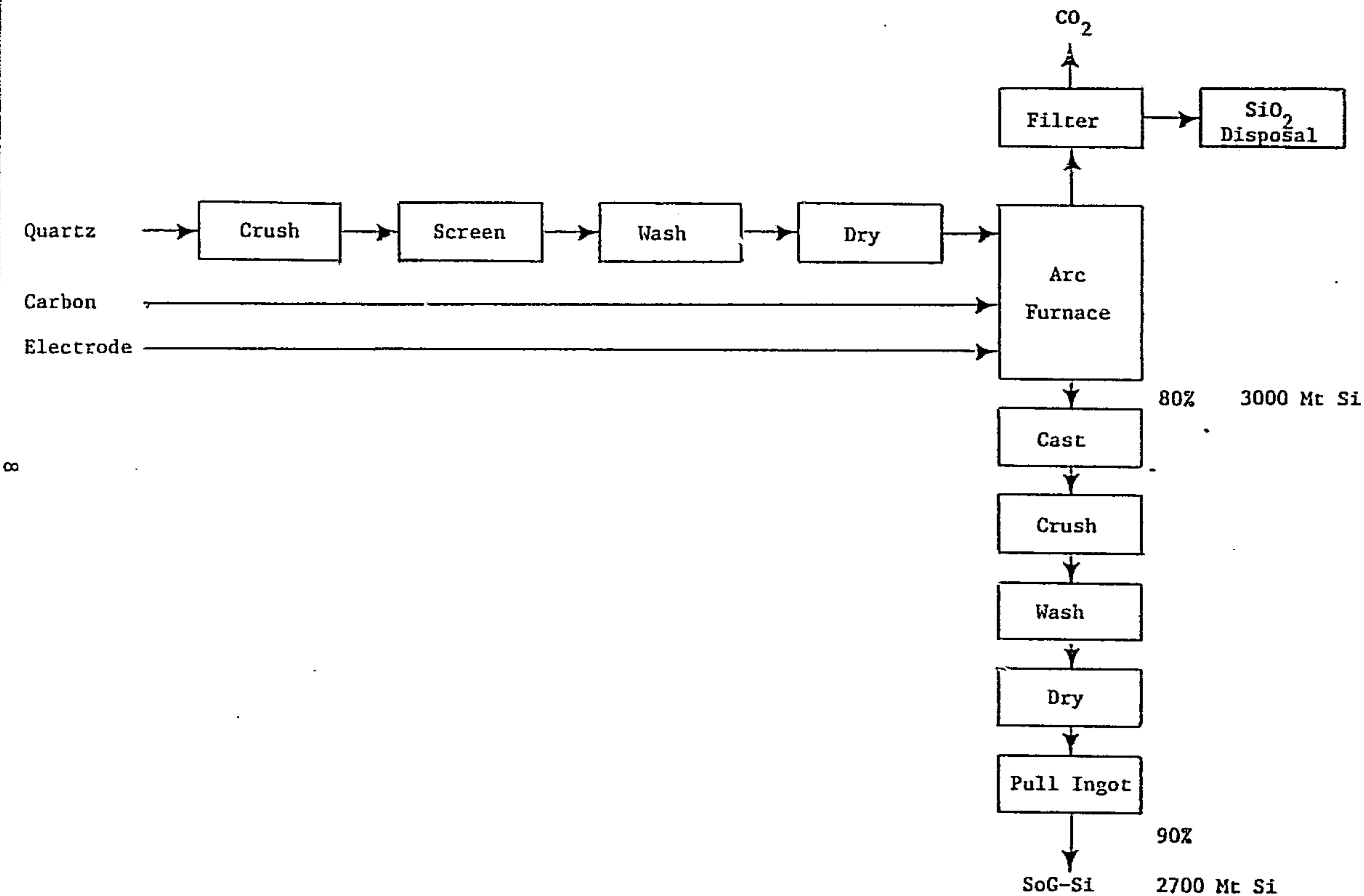



Fig. 2. Outline of Process Flow Diagram for Dow-Corning-Process Silicon.

Figure 3

Cost Analysis of Silicon Production
at a 3000-Mt/y Rate in October 1977 Dollars

CAPITAL COSTS

| | $$\bar{M}$$ |
|---|---|
| Furnace (3000 Mt/y) | 1.7 |
| Recovery System | 0.4 |
| Auxiliary Equip. | 1.2 |
| | 3.3 |

Installed capital = 3 times purchased capital
= \$10 $\bar{M}$

FIXED COSTS

| | $M/y | $/kg |
|---|---|---|
| Labor (25 people) | 500 | 0.17 |
| Maintenance (10%) | 1000 | 0.33 |
| Depreciation (12 years) | 800 | 0.27 |
| Taxes & Insurance (3%) | 300 | 0.10 |
| | 2600 | 0.87 |

VARIABLE COSTS

| | Material Balance (kg mat'l/kg Si) | Price ($/kg) | Cost ($/kg) |
|---|---|---|---|
| Quartz (Arkansas) | 2.70 | $0.20/kg | 0.54 |
| Carbon (Purified Charcoal) | 1.44 | 1.00 | 1.44 |
| Electrodes (Purified) | 0.12 | 1.00 | 0.12 |
| Electric Power | 20 kWh/kg | 0.025 | 0.50 |
| | | | 2.60 |

MANUFACTURING COSTS: \$3.47/kg operating
\$3.33/kg capital

Figure 4

**Cost Analysis of the Dow Corning Process for SoG-Si at a 2700-Mt/y Rate in October 1977 Dollars**

## CAPITAL COSTS

73 machines x $\frac{\$170\ M}{\text{machine}}$ = \$12.4 $\bar{M}$ purchased capital

Installed capital = 3 times purchased capital

= \$37.2 $\bar{M}$ (\$13.78/kg)

## FIXED COSTS

| | \$M/y | \$/kg |
|---|---|---|
| Labor (24 people) | 550 | 0.20 |
| Maintenance (10%) | 3720 | 1.38 |
| Depreciation (7 year) | 5310 | 1.97 |
| Taxes & Interest (3%) | 1120 | 0.41 |
| | 10700 | 3.96 |

## VARIABLE COSTS

| | Material Balance | Price | Cost (\$/kg) |
|---|---|---|---|
| Arc-furnace Si | 1.11 kg/kg | \$3.47/kg | 3.85 |
| Expendables | | | 0.75 |
| Electric Power | 22 kWh/kg | \$0.025/kWh | 0.55 |
| | | | 5.15 |

MANUFACTURING COSTS: \$9.11/kg operating
\$17.10/kg capital

## IV. CONCLUSIONS AND RECOMMENDATIONS

The Dow Corning Process for producing SoG-Si has produced kilogram quantities of silicon. The best of this silicon has been fabricated into solar cells having efficiencies 90 % of baseline cells run as a standard.

A cost analysis of the Dow Corning Process shows that SoG-Si can be produced at about a 3000-Mt/y rate for a manufacturing cost of around $7/kg (January 1975 dollars).

A carbon raw material must be developed which is not only high in purity but also high in reactivity with quartz. An experimental plan has been developed to do this.

It is recommended that short-term resources be spent in developing a suitable carbon material. This must be interfaced with determining its reactivity in an arc furnace and by electrically measuring the purity of the silicon produced after unidirectional solidification.

Once the short-term carbon problem is solved, efforts must be expended on all phases of the program to assure its success. This is particularly true for the unidirectional solidification task in which large capacity (8-10 inch diameter ingot) Czochralski-type machines must be developed for economical silicon purification.

## V. REFERENCES


1. L. P. Hunt, V. D. Dosaj, and J. R. McCormick, "Solar Silicon Via Improved and Expanded Metallurgical Silicon Technology", Quarterly Report No. 4, ERDA/JPL-954559-77/2.

2. Ibid., Quarterly Report No. 2, ERDA/JPL-954559-76/2.

3. Ibid., Quarterly Report No. 4, ERDA/JPL-954559-77/2.

4. Ibid., Quarterly Report No. 5, ERDA/JPL-954559-77/3.

5. Ibid., Quarterly Report No. 3, ERDA/JPL-954559-77/1.

## VI. PROGRAM SCHEDULE

Man-hour and dollar expenditures for this quarter and total to date are shown below.

| | Man-Hours | Dollars |
|---|---|---|
| Past | 5867 | 300506 |
| Current | 699 | 62471 |
| Total | 6566 | 362977 |

The original Program Plan was completed in September 1977.

## VII. PLANS

Future plans were presented in the proposal submitted September 23, 1977.

## VIII. NEW TECHNOLOGY

No reportable items of new technology have been identified.


## IX. ACKNOWLEDGEMENT

Appreciation is extended to L. Crossman, A. Rauchholz, and C. Hendershot of Dow Corning for their assistance in various areas. Significant contributions have also been made by A. Schei of Elkem-Spigerverket A/S.