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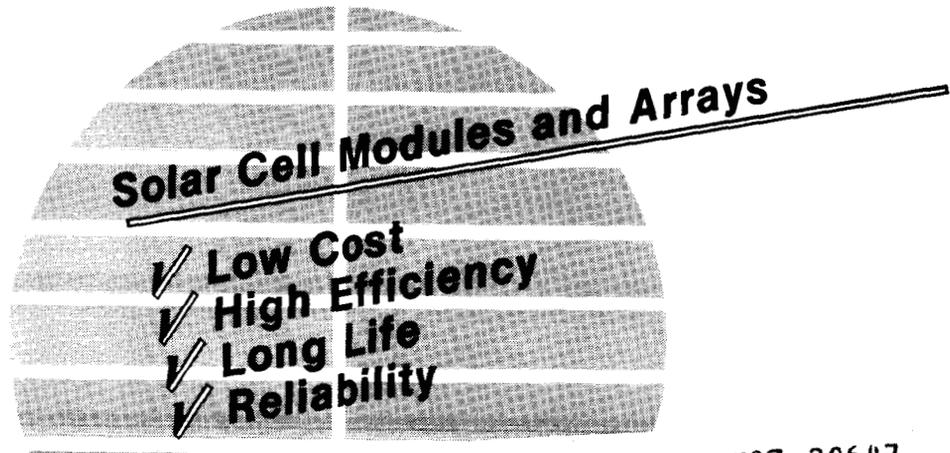
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Electricity from Photovoltaic Solar Cells

Flat-Plate Solar Array Project Final Report

Volume II: Silicon Material

11 Years of Progress



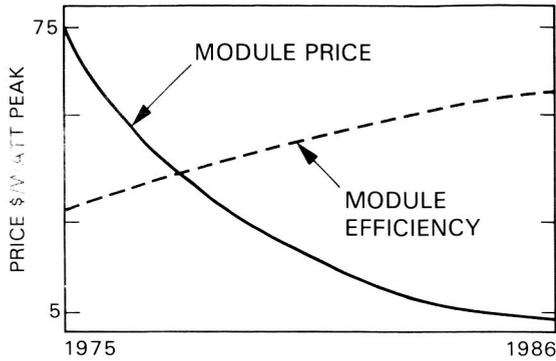
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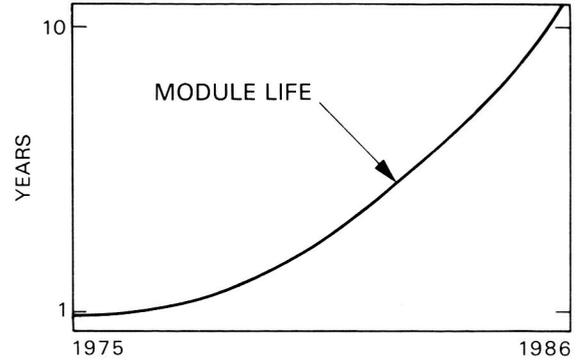
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October 1986

Photovoltaic Module Progress

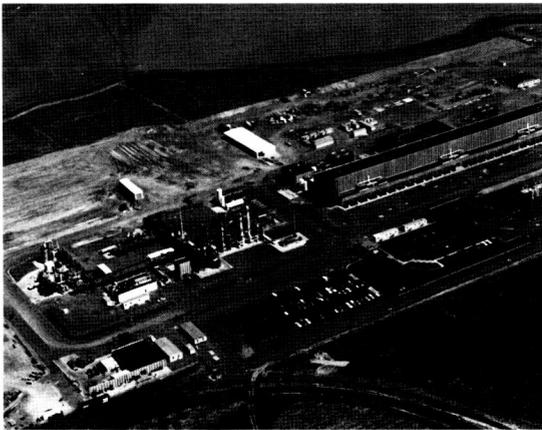


Flat or non-concentrating module prices have dropped as module efficiencies have increased. Prices are in 1985 dollars for large quantities of commercial products.

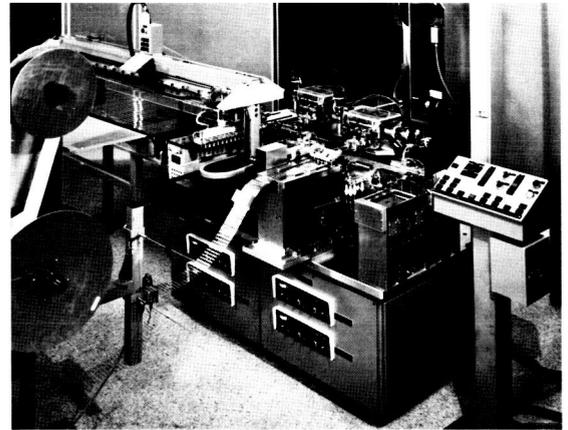


Typical module lifetimes were less than 1 year but are now estimated to be greater than 10 years. (Ten-year warranties are now available.)

Technology advancement in crystalline silicon solar cells and modules (non-concentrating).



Union Carbide Corporation (UCC) funded the now operational silicon refinement production plant with 1200 MT/year capacity. DOE/FSA-sponsored efforts were prominent in the UCC process research and development.



The automated machine interconnects solar cells and places them for module assembly. The second-generation machine made by Kulicke and Soffa was cost shared by Westinghouse Corporation and DOE/FSA.



A Block I module (fabricated in 1975), held in front of four Block V modules, represents the progress of an 11-year effort. The modules, designed and manufactured by industry to FSA specifications and evaluated by FSA, rapidly evolved during the series of module purchases by DOE/FSA.

More technology advancements of the cooperative industry/university/DOE/FSA efforts are shown on the inside back cover. Use of modules in photovoltaic power systems are shown on the outside back cover.

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Solar Array Project

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Electricity from Photovoltaic Solar Cells

Flat-Plate Solar Array Project Final Report

Volume II: Silicon Material

R. Lutwack

11 Years of Progress

October 1986

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JPL Publication 86-31

Final Report Organization

This FSA Final Report (JPL Publication 86-31, 5101-289, DOE/JPL 1012-125, October 1986) is composed of eight volumes, consisting of an Executive Summary and seven technology reports:

- Volume I: Executive Summary.
- Volume II: Silicon Material.
- Volume III: Silicon Sheet: Wafers and Ribbons
- Volume IV: High-Efficiency Solar Cells.
- Volume V: Process Development.
- Volume VI: Engineering Sciences and Reliability.
- Volume VII: Module Encapsulation.
- Volume VIII: Project Analysis and Integration.

Two supplemental reports included in the final report package are:

FSA Project: 10 Years of Progress, JPL Document 400-279, 5101-279, October 1985.

Summary of FSA Project Documentation: Abstracts of Published Documents, 1975 to 1986, JPL Publication 82-79 (Revision 1), 5101-221, DOE/JPL-1012-76, September 1986.

Upon request, this FSA Final Report (JPL Publication 86-31) and the two supplemental reports (JPL Document 400-279 and JPL Publication 82-79) are individually available in print from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Abstract

The Flat-Plate Solar Array (FSA) Project, funded by the U.S. Government and managed by the Jet Propulsion Laboratory, was formed in 1975 to develop the module/array technology needed to attain widespread terrestrial use of photovoltaics by 1985. To accomplish this, the FSA Project established and managed an Industry, University, and Federal Government Team to perform the needed research and development.

The goal of the Silicon Material Task, a part of the FSA Project, was to develop and demonstrate the technology for the low-cost production of silicon of suitable purity to be used as the basic material for the manufacture of terrestrial photovoltaic solar cells. To be compatible with the price goals of the FSA Project, the price of the produced silicon was to be less than \$10/kg (in 1975 dollars).

Summarized in this document are 11 different processes for the production of silicon that were investigated and developed to varying extent by industrial, university, and Government researchers. The silane-production section of the Union Carbide Corp. (UCC) silane process was developed completely in this program. Coupled with Siemens-type chemical vapor deposition reactors, the process was carried through the pilot plant stage. The overall UCC process involves the conversion of metallurgical-grade silicon to silane followed by decomposition of the silane to purified silicon. Production of very high-purity silane and silicon was demonstrated. Although it has as yet not achieved commercial application, the development of fluidized-bed technology for the low-cost, high-throughput conversion of silane-to-silicon has been demonstrated in the research laboratory and now is in engineering development.

A 100-MT/year pilot plant has been in operation since 1983, a 1200-MT/year commercial silane production plant started operation in 1985, and a second 1200-MT/year plant is being checked out and will start up in 1987. A third, larger plant with fluidized-bed reactors (FBRs) for silicon production is scheduled to be operating before the end of this decade. The semiconductor-grade silicon produced in these three plants, all funded by UCC, will constitute about one-third of the world production of silicon for all semiconductor devices.

An economic estimate of the cost of producing silicon by the complete UCC process incorporating FBR technology is \$16.05/kg (1985 dollars). This results in a price of \$25.13/kg that includes a 20% return-on-investment. The goal of the Task was a price of \$18.62/kg. The estimate was made by combining a calculation for the conversion of silane-to-silicon using FBRs with the Lamar analysis (see Section V.D.). The Lamar analysis was modified by deletion of the production section for the use of free-space reactors and melters. It must be kept in mind that these figures are not exact, but are the most recent preliminary chemical engineering estimates.

The other process developments are described to the extent that they were supported by the Project. Some process developments have continued to be developed under private sponsorship.

Studies are reported on the effects of impurities in silicon on both silicon-material properties and on solar cell performance. These studies yielded extensive information and models for relating specific elemental concentrations to levels of deleterious effects.

Foreword

Throughout U.S. history, the Nation's main source of energy has changed from wood to coal to petroleum. It is inevitable that changes will continue as fossil fuels are depleted. Within a lifetime, it is expected that most U.S. energy will come from a variety of sources, including renewable energy sources, instead of from a single type of fuel. More than 30% of the energy consumed in the United States is used for the generation of electricity. The consumption of electricity is increasing at a faster rate than the use of other energy forms and this trend is expected to continue.

Photovoltaics, a promising way to generate electricity, is expected to provide significant amounts of power in years to come. It uses solar cells to generate electricity directly from sunlight, cleanly and reliably, without moving parts. Photovoltaic (PV) power systems are simple, flexible, modular, and adaptable to many different applications in an almost infinite number of sizes and in diverse environments. Although photovoltaics is a proven technology that is cost-effective for hundreds of small applications, it is not yet cost-effective for large-scale utility use in the United States. For widespread economical use, the cost of generating power with photovoltaics must continue to be decreased by reducing the initial PV system cost, by increasing efficiency (reduction of land requirements), and by increasing the operational lifetime of the PV systems.

In the early 1970s, the pressures of the increasing demand for electrical power, combined with the uncertainty of fuel sources and ever-increasing prices for petroleum, led the U.S. Government to initiate a terrestrial PV research and development (R&D) project. The objective was to reduce the cost of manufacturing solar cells and modules. This effort, assigned to the Jet Propulsion Laboratory, evolved from more than a decade-and-a-half of spacecraft PV power-system experience and from recommendations of a conference on Solar Photovoltaic Energy held in 1973 at Cherry Hill, New Jersey.

This Project, originally called the Low-Cost Solar Array Project, but later known as the Flat-Plate Solar Array (FSA) Project, was based upon crystalline-silicon technology as developed for the space program. During the 1960s and 1970s, it had been demonstrated that photovoltaics was a dependable electrical power source for spacecraft. In this time interval, solar-cell quality and performance improved while the costs decreased. However, in 1975 the costs were still much too high for widespread use on Earth. It was necessary to reduce the manufacturing costs of solar cells by a factor of approximately 100 if they were to be a practical, widely used terrestrial power source.

The FSA Project was initiated to meet specific cost, efficiency, production capacity, and lifetime goals by R&D in all phases of flat-plate module (non-concentrating) technology, from solar-cell silicon material purification through verification of module reliability and performance.

The FSA Project was phased out at the end of September 1986.

Acknowledgments

Almost all of the activities of the Silicon Material Task were performed by technical teams under contract as described in this document.

Authorities in the fields of chemical engineering and solid-state physics were used frequently as consultants to provide critiques, to participate in critical technology reviews, and to address important technical problems. Their analyses were decisive for several crucial decisions. Chemical engineering consultants were: Dr. D. Bailey, Traverse City, Michigan; Dr. T. Fitzgerald, Rossmore, California; Professor S. Friedlander, University of California at Los Angeles; Professor O. Levenspiel, Oregon State University, Corvallis, Oregon; Dr. D. Roberts, Menlo Park, California; and Professor C. Yaws, Lamar University, Beaumont, Texas. The solid-state physics consultant was Professor C.T. Sah, University of Illinois, Urbana, Illinois.

Jet Propulsion Laboratory (JPL) engineers involved in laboratory research, technology critiques, process and problem analyses, and the technical management of contracts were: P. Berman, A. Briglio, E. Cleland, R. Cockrum, C. Coulbert, R. Hogle, Dr. G. Hsu, R. Josephs, Dr. H. Levin, Dr. A. Praturi, Dr. R. Rhein, Dr. N. Rohatgi, A. Salama, Dr. P. Seshan, and Dr. A. Yamakawa. In a large part, the progress and control of the technical efforts were the results of their diligence and capabilities.

The successes of the JPL in-house research efforts to develop a silane fluidized-bed technology and material measurement techniques are results of the contributions of the following hands-on technicians: A. Allen, J. Andrews, J. Bell, D. Feller, L. Ford, D. Huls, J. Lloyd and O. McCullogh.

This document reports on work done under NASA Task RE-152, Amendment 419, DOE/NASA IAA No. DE-A101-85CE89008.

FSA Project Summary

The Flat-Plate Solar Array (FSA) Project, a Government-sponsored photovoltaic (PV) project, was initiated in January 1975 with the intent to stimulate the development of PV systems for economically competitive, large-scale terrestrial use. The Project's goal was to develop, by 1985, the technology needed to produce PV modules with 10% energy conversion efficiency, a 20-year lifetime, and a selling price of $\$0.50/W_p$ (in 1975 dollars). The key achievement needed was cost reduction in the manufacture of solar cells and modules.

As manager, the Jet Propulsion Laboratory organized the Project to meet the stated goals through research and development (R&D) in all phases of flat-plate module technology, ranging from silicon-material refinement through verification of module reliability and performance. The Project sponsored parallel technology efforts with periodic progress reviews. Module manufacturing cost analyses were developed that permitted cost-goal allocations to be made for each technology. Economic analyses, performed periodically, permitted assessment of each technical option's potential for meeting the Project goal and of the Project's progress toward the National goal. Only the most promising options were continued. Most funds were used to sponsor R&D in private organizations and universities, and led to an effective Federal Government-University-Industry Team that cooperated to achieve rapid advancement in PV technology.

Excellent technical progress led to a growing participation by the private sector. By 1981, effective energy conservation, a leveling of energy prices, and decreased Government emphasis had altered the economic perspective for photovoltaics. The U.S. Department of Energy's (DOE's) National Photovoltaics Program was redirected to longer-range research efforts that the private sector avoided because of higher risk and longer payoff time. Thus, FSA concentrated its efforts on overcoming specific critical technological barriers to high efficiency, long life, reliability, and low-cost manufacturing.

To be competitive for use in utility central-station generation plants in the 1990s, it is estimated that the price of PV-generated power will need to be $\$0.17/kWh$ (1985 dollars). This price is the basis for a DOE Five-Year Photovoltaics Research Plan involving both increased cell efficiency and module lifetime. Area-related costs for PV utility plants are significant enough that flat-plate module efficiencies must be raised to between 13 and 17%, and module life extended to 30 years. Crystalline silicon, research solar cells (non-concentrating) have been fabricated with more than 20% efficiency. A full-size experimental 15% efficient module also has been fabricated. It is calculated that a multimewatt PV power plant using large-volume production modules that incorporate the latest crystalline silicon technology could produce power for about $\$0.27/kWh$ (1985 dollars). It is believed that $\$0.17/kWh$ (1985 dollars) is achievable, but only with a renewed and dedicated effort.

Government-sponsored efforts, plus private investments, have resulted in a small, but growing terrestrial PV industry with economically competitive products for stand-alone PV power systems. A few megawatt-sized, utility-connected, PV installations, made possible by Government sponsorship and tax incentives, have demonstrated the technical feasibility and excellent reliability of large, multimewatt PV power-generation plants using crystalline silicon solar cells.

Major FSA Project Accomplishments

- Established basic technologies for all aspects of the manufacture of nonconcentrating, crystalline-silicon PV modules and arrays for terrestrial use. Module durability also has been evaluated. These resulted in:
 - Reducing PV module prices by a factor of 15 from $\$75/W_p$ (1985 dollars) to $\$5/W_p$ (1985 dollars).
 - Increasing module efficiencies from 5 to 6% in 1975 to more than 15% in 1985.
 - Stimulating industry to establish 10-year warranties on production modules. There were no warranties in 1975.
 - Establishing a new, low-cost high-purity silicon feedstock-material refinement process.
 - Establishing knowledge and capabilities for PV module/array engineering/design and evaluation.
 - Establishing long-life PV module encapsulation systems.
 - Devising manufacturing and life-cycle cost economic analyses.
- Transferred technologies to the private sector by interactive activities in research, development, and field demonstrations. These included 256 R&D contracts, comprehensive module development and evaluation efforts, 26 Project Integration Meetings, 10 research forums, presentations at hundreds of technical meetings, and advisory efforts to industry on specific technical problems.
- Stimulated the establishment of a viable commercial PV industry in the United States.

Silicon Material Summary

The objective of the Silicon Material Task was to develop processes capable of large-scale production of polysilicon,* suitable for the fabrication of photovoltaic (PV) solar cells, at costs commensurate with a market price of less than \$10/kg (1975 dollars). The efforts, involving teams of scientists and engineers under contract, consisted of:

- (1) Research and development of 11 alternative processes (Table I).
- (2) Support activities in the areas of chemical engineering, economic analyses, and material characterization (Table II).
- (3) Investigations of the effects of impurities on the performance of solar cells used for evaluating process purification requirements and economics (Table III).

The process development phases were:

- (1) Demonstration of technical feasibility of processes by studies using small-scale, primary process reactors.
- (2) Characterization of operating conditions of scaled-up process units, assessment of process production and economic potentials, determination of steady-state operating conditions of integrated sections of process equipment, and optimization analyses.
- (3) Establishment of operating capabilities of complete processes in pilot plants.
- (4) Operation of large-scale production plants.

As calculated from various U.S. Department of Energy projections for the PV solar cell industry, several modifications of the Task program and schedule were formulated to meet perceived modified demands for polysilicon production. The basic program, leading to a large-scale production plant in 1986, remained the Task's guideline, until funding restrictions, beginning in 1981, forced the deletion of the large-scale production plant phase and limited the scope of the program to the development and pilot plant demonstration phases.

Table I. Process Development Contractors

Process	Contractor	Start	End
Zn/SiCl ₄ fluidized bed	Battelle Columbus Laboratory	10/75	1/81
SiH ₄	Union Carbide	10/75	4/86
Na/SiF ₄ chemical vapor transport	Motorola	2/76	10/79
SiO ₂ /C thermal plasma	Texas Instruments	2/76	1/77
Na/SiF ₄ gas phase reaction	SRI International	6/76	2/80
Non-equilibrium plasma jet	Aerochem Research Lab	7/76	10/78
SiO ₂ /C direct arc furnace	Dow Corning	7/76	10/78
Na/SiCl ₄ arc heater	Westinghouse Electric	10/76	12/79
Na/SiCl ₄ flame	Aerochem Research Lab	5/77	2/81
Bomosilane fluidized bed	J.C. Schumacher	10/77	11/78
SiH ₂ Cl ₂ CVD	Hemlock Semiconductor	10/79	5/83

* The term "polysilicon" as used in this report refers to high-purity, polycrystalline silicon.

Table II. Support Programs Process Developments

Contract Title	Contractor	Start	End
Studies of Process Economics	Lamar University	10/75	2/81
Hydrochlorination of mg-Si	Massachusetts Institute of Technology	3/79	4/81
Particle growth from SiH ₄ in a free-space reactor	California Institute of Technology	9/80	1/86
Studies of process economics	Texas Research and Engineering Institute	5/81	7/82
Hydrochlorination of mg-Si	Solarelectronics	7/81	4/83
Model of SiH ₄ - fluidized-bed reactor	Washington University at St. Louis	12/83	12/84
Radiantly heated fluidized bed	Oregon State University	9/82	8/83

Table III. Studies of Impurity Effects

Contract Title	Contractor	Start	End
Determination of definition of solar-grade silicon	Monsanto	10/75	9/76
Effects of impurities and processing on silicon solar cell performance	Westinghouse Research Center	10/75	2/82
Lifetime and diffusion length measurements	Northrup Research Center	12/76	11/77
Measurements of impurity effects	Spectrolab	2/77	12/77
Effects of impurities on silicon solar cell performance	C.T. Sah Associates	2/77	—
Composition analyses of doped silicon	National Bureau of Standards	4/77	1/79
Composition measurements by photon catalysis	Aerospace	10/78	9/79
Measurements of effects of impurities	Solarex	1/79	1/80
NAA measurements of doped silicon	Lawrence Livermore Lab	8/83	9/85

Key Accomplishments

The major success of the Task activities was the complete demonstration of steady-state silane production in the Union Carbide Corp. (UCC) silane process in a 100-MT/year Experimental Process System Development Unit (EPSDU). An EPSDU is the equivalent of a pilot plant. Based on EPSDU technology, a 1200-MT/year plant, funded by UCC, began operation in 1985; the second 1200-MT/year plant is projected to be in operation in 1987. The silane and polysilicon products of these plants have been shown by analyses to be purer than semiconductor grade. The silane will meet a growing demand for feedstock for the fabrication of amorphous silicon devices as well as for other purposes.

The most recent UCC estimate (in 1985 dollars) for the conversion of silane-to-silicon by fluidized-bed reactors (FBRs) is based upon the use of four quartz-lined, 12-in.-diameter FBRs in a 1000-MT/year plant. The calculation yielded an incremental product cost of \$6.10/kg of silicon and a price at 30% discounted cash flow of \$10.26/kg silicon. The FBR section of the plant requires a total investment of \$7.2M, and an annual operating cost of \$5.53M.

To obtain an estimate of the overall product cost, these data were combined with the early economic analysis prepared by Lamar University investigators (see Section V.D.). The Lamar analysis was modified by the deletion of the costs for the conversion of silane to molten silicon in the process that uses free-space reactors. A calculation, using the UCC silane-to-silicon FBR data and the modified Lamar analysis, results in estimated overall product costs of \$8.73/kg silicon (1975 dollars) and \$16.05/kg silicon (1985 dollars). The corresponding prices that include a 20% return-on-investment are \$13.66 and \$25.13/kg, respectively. It must be kept in mind that these figures are not exact, but are the most recent preliminary chemical engineering estimates.

The silane-to-silicon conversion units in these UCC installations are Siemens-type Chemical Vapor Deposition (CVD) reactors, that are not capable of the high-throughput, low-energy-use operation needed for the low-cost production of polysilicon. Thus, the silane-to-silicon conversion, using a FBR, was developed to attain the abovementioned desirable production characteristics. This FBR research and development (R&D) was done in collaborative programs in the laboratories of the Jet Propulsion Laboratory (JPL) and UCC. At JPL, the silane concentration limit for silicon deposition was extended in the FBR operation, most experiments being done in the 40 to 60% range; sometimes concentrations of 80 and 100% were used. The reactor operation was controlled to obtain a conversion efficiency of essentially 100%, with 90% deposition on the seed particles in the bed while limiting the elutriation loss of fine particles to less than 10%. The maximum production rate was 3.5 kg/h, and a product removal rate of 3 kg/h was demonstrated. An empirical deposition model also was formulated. A computer model of the silane FBR was developed under contract at Washington University at St. Louis.

The main objective in the UCC program was to obtain a database for an engineering design. Many long-term runs, ranging up to 80 h, were successfully conducted using silane feed concentrations between 20 and 25%. The deposition-efficiency data were approximately the same as obtained at JPL. These results led to preliminary descriptions of the reactor design and the operating conditions for a large-scale production reactor.

Varying levels of technological maturity were obtained in the other process-development contracts of the Task. In some cases, partial technical success was achieved with collections of data for material properties and for reaction kinetics and yields, or with reactor designs, or with the operation of small process development units. The most successful of these developments have been advanced further with non-Government funding after contracts for them were deleted from the Task. These developments are:

- (1) Dichlorosilane-CVD process by Hemlock Semiconductor. A higher throughput and yield at a lower energy use compared to conventional Siemens trichlorosilane process were demonstrated under the JPL contract.
- (2) Gas-Phase Sodium Reduction of Silicon Tetrachloride Process by Aerochem Research Laboratories. Continued development at AeroChem Research laboratories and Universal Silicon has resulted in increased silicon purity and throughput for this very low energy-use process.
- (3) Carbothermic Reduction of Silica in an Arc Furnace by Dow Corning. Improvements in purity levels and large-scale metallurgical reactions have been obtained in continued developments by Elkem-Exxon, Solarex, and Elkem.
- (4) Sodium-Reduction of Silicon Tetrafluoride by SRI International. Material and solar cell data indicating improved product purity have been reported.
- (5) Bromosilane Process by J.C. Schumacher. Plans for the installation of a pilot plant and the design of a production plant were announced by Schumacher in 1985.

The R&D efforts to fully develop these processes with private funding show technology transfer has taken place from the Task to industry.

Extensive studies of the effects of impurities on cell performance by the Westinghouse Research Center and Professor C.T. Sah, along with supporting efforts for cell evaluations and material characterization, have provided a large body of information and models for relating specific, impurity-element concentrations to levels of deleterious effects on cell performance. Impurity effects were shown to be species-dependent with the group of tantalum, zirconium, molybdenum, tungsten, niobium, vanadium, and titanium causing degradations of 5 to 10% in cell performance at concentrations of 10^{-6} to 10^{-5} ppma. Increased sensitivity to impurities was found for cells with high-base diffusion lengths and for high-efficiency cells. To prevent single crystal structure breakdown during growth, the allowable total impurity concentration in the silicon feedstock is required to be in the range of 200 to 500 ppma. The tolerable total impurity concentration,

being dependent on the crystal growth procedure, must be selected to suit the specific growth process while concurrently taking into account the desired solar cell energy conversion factor and the effects of particular elements. Concentrations of boron and phosphorus also must be tightly controlled, because the yield of usable crystal with the desired resistivity range depends directly on initial concentrations of these elements.

Thus, these studies demonstrated that separate definitions of a solar-cell-grade polysilicon material are required to meet specific conditions. An analysis must be done to take into account the effects of specific elements, of total impurity concentration, of boron and phosphorus concentrations, and of crystal and cell processing procedures. These must be balanced with desired cell performance characteristics and economics. Experimental and theoretical results from this program have been used worldwide by groups developing polysilicon processes, by commercial polysilicon producers and by the PV solar cell industry.

The main Task program was supported by:

- (1) Contractual efforts with private and Government laboratories.
- (2) Consultants who are recognized authorities in their fields of expertise (Table IV).
- (3) Chemical engineering and economic analyses.
- (4) Impurity concentration measurements.
- (5) In-depth process assessments.

The JPL group also was active in these technical areas. The information, conclusions, and innovations derived in the Task program have had a worldwide effect on R&D activities and polysilicon production plans.

Table IV. Consultants

Chlorosilane and Silane Chemistry

Dr. D. Bailey, Consultant

Chemical Engineering

Dr. T. Fitzgerald, Oregon State University (TRW)*

Professor S. Friedlander, California Institute of Technology (University of California at Los Angeles)*

Dr. D. Roberts, California Institute of Technology (SRI International)*

Professor O. Levenspiel, Oregon State University

Professor C. Yaws, Lamar University

Solid State Physics

Professor C.T. Sah, University of Illinois

* Present affiliation.

Technology Still Required to Achieve Task Goal

The Task goal will be achieved upon completion of a silane-FBR development that demonstrates the production practicality of the UCC Silane Process. An engineering design must be obtained of a FBR capable of yielding semiconductor grade silicon in a high-volume throughput with low energy-use and low-cost operation. This will require: (1) solutions of the main technical problems of the preparation of pure seed particles, (2) the prevention of contamination during deposition, and (3) the capability for long-term, steady-state operation.

The Task goal may also be reached if production practicality is demonstrated for any of the former Task process developments that now are being developed further. These require varying levels of continued development.

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SECTION I

Introduction

A. OBJECTIVE AND GOALS OF THE SILICON MATERIAL TASK

In 1975, under contract to the U.S. Government, the Jet Propulsion Laboratory (JPL) had formed the Low-Cost Silicon Solar Array (LSSA) Project to develop the technology needed to achieve widespread terrestrial use of photovoltaic (PV) solar arrays by 1985. The Project's name was later changed to the Flat-Plate Solar Array (FSA) Project. The JPL-managed FSA Project was a cooperative effort of industrial, university, and Government scientists and engineers to attain the Project's research and development (R&D) goals.

As part of the FSA Project, the Silicon Material Task had as its objective the development and demonstration of the technology for the low-cost production of silicon of a purity suitable enough to serve as the basic material in the manufacture of PV solar cells for terrestrial uses.

The three goals of the Silicon Material Task were to develop processes for the production of silicon:

- (1) Of a purity adequate for the manufacture of single crystalline-silicon solar cells that meet the requirements of the FSA Project.
- (2) At a market price of less than \$10/kg (in 1975 dollars). This is equivalent to a market price of \$19/kg (in 1985 dollars).
- (3) In high-volume production plants (more than 1000 MT/year).

B. EFFORTS OF THE SILICON MATERIAL TASK

The Silicon Material Task consisted of three primary activities:

- (1) Development of low-cost processes for the production of semiconductor-grade and solar cell-grade (less pure) silicon.

- (2) Study of the effects of impurities in silicon on material properties and the performance of solar cells.
- (3) Carrying out theoretical and experimental investigations ancillary to the efforts of (1) and (2), above.

C. ORGANIZATION OF THE REPORT

Section I provides a description of the Task's programs and schedules, formulated in response to changes in objectives and resources.

Section II describes the history, background, and implementation of the Silicon Material Task Program.

Section III deals with the investigations of three processes directed toward the goal of producing low-cost semiconductor-grade silicon.

Section IV consists of descriptions of eight separate process developments with the goal of producing low-cost solar-grade silicon, which is less pure than semiconductor-grade silicon, but suitable for meeting the Project's energy conversion efficiency goal.

Section V describes the chemistry, chemical engineering, and economic studies supporting the primary process development efforts.

Section VI consists of descriptions of efforts to determine the effects of impurities on the properties of silicon and on the energy conversion efficiency of solar cells. This information was intended to form the basis for analyses of the requirements for purification units and the associated economics for specific processes.

Section VII deals with the research efforts carried out at JPL. This research was in the areas of chemical engineering and of silicon material properties.

A summary of the Task program is given in Section VIII.

Publications that describe the results of the Task efforts are listed in Appendix A.

SECTION II

History, Background, and Implementation of the Silicon Material Task Program

A. SOLAR ENERGY CONFERENCE AT CHERRY HILL, NEW JERSEY

The Conference on Photovoltaic Conversion of Solar Energy for Terrestrial Applications was held in October 1973 at Cherry Hill, New Jersey. One of the recommendations adopted by the Single-Crystal Silicon Solar Cell Workshop at the conference was to initiate a program to develop a low-cost process for the production of polysilicon. The program eventually was to lead to the installation of a commercial plant to produce polysilicon.

B. SCHEDULE FOR THE SILICON MATERIAL TASK

In January 1975, the FSA Project began at JPL under its original name of the Low-Cost Silicon Solar Array (LSSA) Project. As one of the five technical tasks of the FSA Project, the Silicon Material Task originally had the following schedule:

- (1) By end of FY 76: to define the process to produce polysilicon.
- (2) In FY 79: to have an operating pilot plant.
- (3) In FY 83: to have a large-scale, operating, production plant.

By February 1975, the schedule for (1), (2), and (3), above, was delayed 1 year to FY 77, 80, and 84, respectively.

In January 1975, JPL sent a letter of interest describing specific R&D efforts and program phases to universities, research laboratories, and industry. At that time, the Silicon Material Task was divided into the following four phases (Table 1):

- (1) Phase 1: Evaluation of technical problems and potential capabilities of proposed candidate processes. Selected processes were to be characterized by experimental studies. To determine the effects of impurities on material properties and solar cell performance, a subtask to establish specifications for solar-cell-grade silicon was to be carried out concurrently.
- (2) Phase 2: Extensive experimental investigations to be carried out with scaled-up reactors.
- (3) Phase 3: Pilot plants to be installed, based upon those processes selected as having the highest potential.

- (4) Phase 4: Construction and operation of large-scale, commercial production plants.

Table 1. Task Structure

Process developments
Phase I : Technical feasibility
Phase II : Scale-up experiments
Phase III: Experimental process system development units
Phase IV: Large-scale production plants
Process developments: supporting subtasks
Effects of impurities
Materials of construction
Composition analyses
Economic analyses
Theoretical and experimental chemistry
In-house experimental program
JPL analysts
Consultants
Chemical processing
Chemical engineering
Solid state physics

C. IMPLEMENTATION OF THE SILICON MATERIAL TASK

These considerations led to construction of a 10-year Silicon Material Task program based on the development of production processes for both semiconductor-grade and solar-cell-grade silicon.

Because of the constraint to have a large-scale plant on-stream by mid-1984, the schedule committed only 12 months to determine process feasibility. The period for obtaining and analyzing scale-up data was given 18 months, and pilot plant design and construction was allotted 2-1/4 years. The decision on which a specific process was to be used in the large-scale plant was set for October 1981, with the plant's completion in August 1984.

However, at the request of the Energy Research and Development Administration (ERDA) to arrange for increased polysilicon production earlier than had been planned previously, the Task program was modified in May 1977 to accelerate the schedule to ensure additional polysilicon availability from 25-MT/year experimental production facilities to be operational in January 1981. The revised schedule, requiring the diversion of technical effort and resources, forced a delay

until June 1986 for the milestone to have an operational large-scale production plant. Table 2, in which the production goals of the accelerated plan are compared to the basic Task plan, shows the effects of various Government plans on the estimates of polysilicon requirements for the U.S. PV solar cell industry. Incremental increases in polysilicon requirements were calculated on the basis of a solar cell production schedule of 4 MW in FY 79, 8 MW in FY 80, 15 MW in FY 81, and 25 MW in FY 82, using the assumption of 12% efficient arrays, 0.025-cm-thick cells, 100 mW/cm² incident power, and an overall 40% silicon utilization in array fabrication.

In June 1977, a critical review of the Task program and of the general problems that could be encountered in developing new polysilicon processes was held. The group of experts consisted of Dr. Don Bailey of Union Carbide Corp. (UCC), Dr. John Blocher of Battelle Columbus Laboratories, Professor Thomas Fitzgerald of Oregon State University, Dr. Henry Gutsche of Monsanto, Dr. Lee Hunt of Dow Corning, Dr. Erhard Sirtl of Wacker-Chemitronic, and Professor Carl Yaws of Lamar University. The Project was represented by John Goldsmith (Deputy Project Manager), Dr. George Hsu, and Dr. Ralph Lutwack (Silicon Material Task Manager).

The review discussions dealt with the following topics:

- (1) Potential usefulness of the Siemens Process technology for low-cost polysilicon production.
- (2) Estimates of production requirements to meet the needs of the Project's program.
- (3) Possible use of material less pure than semiconductor-grade silicon for PV solar cells for terrestrial applications.
- (4) Probable technical advantages of the new processes currently being developed in the Task program.
- (5) Structure of the Task program.

The following general conclusions were defined:

- (1) The Task program plan was appropriate for meeting the Task's objectives.

- (2) The Project's economic goals could not be met by a process that incorporated chemical vapor deposition (CVD) reactors.
- (3) Results derived from studies on impurity effects should be disseminated quickly to the silicon technical community.
- (4) Materials of construction should be investigated separately in the Task program, because serious problems were likely to occur in different chemical regimes. The group concurred in the desire to have similar meetings in the future and to invite a wider attendance.

D. CHANGES IN THE SCHEDULE TO ACCELERATE PRODUCTION OF POLYSILICON

A much more intense schedule for producing polysilicon for an interim period covering FY 80 through FY 83 resulted from the goals of the U.S. Department of Energy (DOE) Plan of 1979. The preliminary Task plan to meet these goals (see Table 2) necessitated the addition of a subprogram for the development of the technology and the installation of production facilities to provide polysilicon for the interim demands while maintaining the basic Task program geared to the 1986 objective of installed 6000-MT/year capacity. Because the common, conservative chemical engineering approach undoubtedly was not applicable for the precipitous build-up of production capacity based on untried processes, opinions were solicited from the technical managers of some of the process development contracts. Concepts and proposed plans for accelerated schedules were discussed in joint meetings of DOE, JPL, and the managers of the Battelle, Dow Corning, UCC, and Westinghouse contracts.

One of the contractors proposed a very conservative plan involving the meeting of short term (1982) needs by buying polysilicon at the current prices and stockpiling to meet future demands. To meet the needs for the intermediate period of 1981 to 1986, the proposed solution was to modify and optimize the trichlorosilane (SiHCl₃)-Siemens process, enabling an estimated polysilicon cost of \$30 to \$38/kg (1975 dollars). Long-term needs beyond 1986 were to be met either by the installation of a newly developed process with a projected cost (\$10/kg, or by a radically modified SiHCl₃-Siemens process with a projected cost of about \$25/kg

Table 2. Projected Requirements For Silicon (metric ton/year)

	FY	78	79	80	81	82	83	84	85	86	87	88
Task Plan ^a		3.6	7.8	12	14	36	48			6000		
Accelerated Plan ^a		18	48	96	180	300						
Marvin Plan ^a				240	480	900	1500					
McCormack Bill ^b			47	89	167	312	583	1080	2000	3665	6670	12000

^aCalculated on the basis of 12% energy conversion efficiency, 0.025-cm-thick cells, 0.1-w/cm² incident power, and 40% silicon utilization.

^bCalculated using a linear decrease in metric tons/MW from December 1 to June 1, FY 79 through FY 88. Silicon production in FY 88 to meet 2000 MW produced in FY 88. Array production doubled each year through FY 88.

(1975 dollars). A 500- to 1500-MT/year plant using modified Siemens technology was projected to be operational in 1982 and a 3000-MT/year plant would be in operation in 1986 if an accelerated program was implemented. The schedule projections for plants based on new technology were for 300- to 1500-MT/year capacity by late 1982 and for 3000-MT/year capacity by early 1985.

A second contractor proposed two plans:

- (1) Production units for a process under development were to be placed on-stream incrementally and periodically so that capacities of 100 MT/year in 1980, 500 MT/year in 1981, and 1000 MT/year in 1982 would be attained. The estimated average cost of the produced silicon was \$14/kg, and the 1000-MT/year plant was estimated at \$10/kg (1975 dollars).
- (2) The concurrent operation of five 100-MT/year plants was to be used to produce 500 MT/year of silicon at an estimated \$32/kg (1975 dollars).

Four sizes of plants were incorporated into the plan proposed by a third contractor. After early process verification in December 1979, a 250-MT/year facility would be in operation by December 1980 followed by 500 MT/year in December 1981. Large-scale plants of 1000-MT/year and 1500-MT/year capacities would then be designed, installed, and operated by December 1982 and December 1983, respectively. Product cost estimates (\$/kg) for 500-, 1000-, 1500-, and 3000-MT/year plants were given as \$13.60, \$9.75, \$8.40, and \$7.20 (1975 dollars), respectively.

A fourth contractor discussed three accelerated schedules involving a comprehensive chemical engineering analysis. Each schedule would lead to less certain, higher risk, process designs and programs because of the sacrifice of a conservative database for the process design. Although successful production of polysilicon was likely in each case, production under non-optimized conditions would be less efficient in material and energy uses as well as leading to lower product yield and higher product cost. The three proposed options were:

- (1) A so-called aggressive schedule would enable an operational start of a 1500-MT/year plant at the first of 1985 rather than early 1986. This would involve saving time because of a shorter procurement period and would have the experimental operation of the 25-MT/year (or 50-MT/year) Process System Development Facility (PSDF) be concurrent with the effort to design the large plant.
- (2) A so-called accelerated schedule, in which the activities for the design, detailed engineering, procurement, fabrication, and construction of the PSDF and the large-scale plant would run nearly concurrently. This would allow a production start of 600 MT/year in 1982 and 1500 MT/year in 1983.

- (3) A non-PSDF program, in which the development of major units of the process would be continued instead of installing the PSDF. This is a process development approach that sometimes is used commercially, keeping in mind that the elimination of PSDF data for steady-state operation may result in increased risk for successful operation of the large-scale plant. This specific variation of an accelerated schedule option would likely allow a 1500-MT/year plant to be operating by 1983.

These accelerated schedules should be compared with the basic 1977 Task schedule: design start for the PSDF in January 1978, 1-1/2 years of operation of the PSDF, and design-start of the 6000-MT/year plant for June 1982 with operation in June 1986.

Another Task plan was devised to conform to the requirements of the congressional McCormack bill. This bill mandated a yearly doubling of solar cell array production starting with 4 MW in FY 79 and increasing to 12000 MW in FY 88 (see Table 2 and Figure 1). The required polysilicon production was calculated (see Table 2) based on a linear decrease in polysilicon utilization from 12 MT/MW to 6 MT/MW during this period as a consequence of improved sheet and cell fabrication technology. The revised plan, shown in Figure 1, discloses the stringent schedule, especially for the process and pre-experimental process system development units (EPSDU) stages. The very large risks inherent in this plan were strong arguments against its adoption in the Task program.

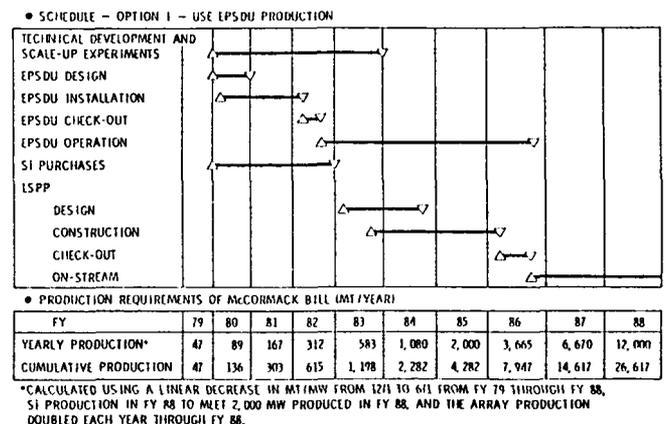


Figure 1. Proposed Program to Meet McCormack Bill

Restructuring of the Task took place in mid-1978 when the concept that the price reduction goal could not be reached by economies-of-size or evolutionary modifications of the conventional Siemens process had been substantiated by an economic analysis by Lamar University.

E. PROCESS CONTRACTS AWARDED BASED UPON TECHNOLOGICAL MATURITY

After an analysis comparing the development status of each of the process contracts with the Task schedule, the contracts were divided into two general

groups based on the evaluations of relative technological maturity. In the first group, the basic chemistry studies and much of the chemical engineering experimental and analysis phase had been completed, and an ambitious schedule for full-scale production plants in 1986 was considered to be appropriate. Scale-up investigations for the primary reactor units of the processes were already underway to obtain data for further chemical engineering and optimization calculations as well as for designs of EPSDUs (sized to about 100 MT/year). Concurrently, calculations and preliminary designs were being done for the EPSDU.

The developments for the Silane Process by UCC, and for the Zn-SiCl₄ Process by Battelle Memorial Institute were placed in the first category. In the Silane Process effort, each of the process steps leading to high-purity silane (SiH₄) had been developed to the stage enabling the initiation of preliminary process designs. Data to be used for the optimization and the final design of the process were being gathered. The UCC contract schedule was directed to achieving the mid-1986 objective of an on-stream operation of a large-scale production plant. A preliminary economic analysis by UCC provided an encouraging cost value of \$7.80/kg (1975 dollars) silicon, based on the use of a free-space reactor (FSR) to convert silane to silicon.

The immediate objectives of the Battelle Zn-SiCl₄ contract were to increase the conversion efficiency and to develop a continuous process. While conducting the experimental development, a preliminary large-scale process design and design of a 50-MT/year EPSDU were completed. Projection from the contract schedule indicated a 1985 start for the on-stream operation of a large-scale plant. Estimates of the total product cost, made by Battelle and by Lamar University, ranged from \$9.12 to \$9.50/kg (1975 dollars) silicon for a closed-loop process.

The second group of activities in the Task plan contained process developments that had the potential to achieve the Task's goals, but which were at a relatively immature stage of technology development. In these cases, chemical and chemical engineering data were being obtained for the purpose of demonstrating technical feasibility. These developments were being carried out by Westinghouse, Dow Corning, Motorola, Stanford Research Institute (SRI) International, and AeroChem Research Laboratory.

The 1978 Task plan proposed a sequence of milestones for reducing the number of processes being developed under contract at different stages. This plan required:

- (1) Seven process developments be continued at the start of FY 79.
- (2) Four processes be selected to proceed with EPSDU designs at the beginning of FY 80.
- (3) The design and construction periods for the EPSDUs be overlapped allowing the interval

for the detailed engineering designs to be concurrent with the site preparation and early EPSDU construction.

- (4) The EPSDU operation be overlapped with the interval for the design and first stage of the construction of two large-scale production plants.
- (5) On-stream operation of the large-scale plants take place by the end of FY 86.

If the developments of the first group were successful, the schedule for the Battelle 50-MT/year EPSDU was to be the second quarter of FY 81, and the UCC 100-MT/year EPSDU would be the first quarter of FY 82.

The proposed modified Task plan, formulated in response to the DOE request to outline the changes needed to meet adjusted polysilicon production goals for the FY 81 to FY 86 period, included an intact primary plan to achieve the FY 86 Task objective. There was considerable uncertainty, however, as to the capability of an EPSDU to produce acceptably uniform, pure product following the suggested production schedule. The conflict stemmed from the recognition that the experimental nature of the EPSDU was unsuitable for commercial production. The EPSDU was intended to secure engineering data for describing steady-state operating conditions, for optimization calculations, and for process design.

It seemed likely that sacrifices of production efficiency would result in lower yields as well as higher production costs and energy use. Also, the technology development would be at a higher risk as consequences of accelerated production schedules and concomitant decreased databases before plant design. To ameliorate these difficulties in preparing the plan, production efficiency factors were applied in the calculations of the production capacity values. Two options of modified schedules were formulated and proposed. Each option contained continuations of the process experimental studies and of the various supporting efforts for impurity-effect studies, ancillary engineering investigations, and consultant analyses. The first option was based on the use of processes being developed by Battelle and UCC; the size of the UCC EPSDU was increased to 250 MT/year. The Westinghouse process was included in the second option, with the capacity of the UCC EPSDU set for 100 MT/year.

F. THE EXPERIMENTAL PROCESS SYSTEM DEVELOPMENT UNIT PROGRAM

The primary objective of the FY 80 plan was to begin the EPSDU program. The approach included the following efforts:

- (1) To conduct critical reviews of the technology status of candidate processes.

- (2) To initiate fabrication and procurement actions for EPSDU construction.
- (3) To continue R&D programs for theoretical and experimental studies of reactors and sub-systems.
- (4) To operate process development units (PDUs) consisting of integrated subsystems to characterize the effects of equipment modifications and operating parameters.
- (5) To intensify the studies of impurity effects.

The budget limited the FY 80 Task program to two EPSDUs. One EPSDU was for the UCC Silane Process. R&D efforts to develop other processes to the EPSDU stage were continued, although none of them could meet the 1982 goal of Technical Readiness. At the start of FY 80, developments were underway at Battelle, Westinghouse, SRI International, Hemlock Semiconductor Corp. (HSC), and AeroChem Research Laboratories. Developments at SRI and Westinghouse were terminated during FY 80. Critical reviews of the competing process developments were scheduled. The Silane Process development was emphasized in the Task program and was being supported by:

- (1) An investigation of the hydrochlorination reactor at the Massachusetts Institute of Technology (MIT).
- (2) Chemical engineering and economic analyses at Lamar University.
- (3) The JPL in-house modeling and experimental studies of the continuous flow pyrolyzer (CFP) and of the fluidized-bed reactor (FBR).

Research on the effects of impurities on cell performance was continued by the Westinghouse Research Center and Professor C.T. Sah.

FY 81 was to be the second year of the undertaking for the Silane Process EPSDU. Key milestones for this effort included the start of construction, the completion of the installation drawings package, the fabrication and delivery of the major equipment, and a critical review of the FBR development. A sharp reduction in the FY 81 FSA Project budget, however, severely reduced the funding allocation for the EPSDU. In March 1981, this forced the issuance of a series of stop-work orders and revised work statements for the SiH_4 pyrolysis and silicon deposition investigations. These actions were taken in efforts to maintain the main EPSDU program. When further cut-backs were enforced, however, it became obvious that the completion of the installation was not possible.

At this time, many activities of the EPSDU program were either completed or were nearing completion: (1) the EPSDU process design package had been completed; (2) the EPSDU site at East Chicago, Indiana, had been prepared; (3) all of the equipment, except the

deposition reactor and a few minor items, had been delivered; and (4) much of the major equipment had been installed in the gantry. Only the mechanical installation and the electrical work remained to be done.

A series of meetings involving UCC, JPL, and DOE were held to explore options for the UCC contract and to devise a strategy to enable the completion of the EPSDU program. The available information indicated DOE funding for FY 82 and FY 83 would also be inadequate. Thus, because the EPSDU program could not be completed without substantial cost-sharing by UCC, the discussions centered on how to accomplish this. The only mutually agreeable option obligated UCC to complete the installation, to check it out, to start it up, and to operate the EPSDU for at least 1 year. In return for the transfer of the title of the EPSDU equipment to UCC, the company would supply a final report describing the modifications undertaken and the operation of the facility for 1 year. Data for the silane-to-silicon conversion step were not to be provided because a proprietary deposition reactor, licensed from Komatsu Electronic Materials, Inc., was to be used in the EPSDU. Under this transfer-of-title arrangement, UCC was required to pay all of the costs involved in the removal and shipment of the equipment to the selected site at Washougal, Washington, in the restoration of the site at East Chicago, Indiana, and in the installation and operation of the EPSDU. The FSA Project agreed to continue funding of FBR development. A careful JPL analysis indicated this arrangement would oblige UCC to spend in excess of \$6.4M in exchange for the title to equipment costing \$2,765,655. The EPSDU transfer to Washougal, Washington, was authorized by JPL in September 1981.

G. THE UCC SILANE-FBR AND THE HSC DICHLOROSILANE-CVD PROCESSES

During FY 81, process development at Battelle was terminated. Thus, in addition to the UCC EPSDU, the only active process development program remaining was the SiH_2Cl_2 -CVD process development of HSC. The engineering and economic analysis of this process development, originally underway at Lamar University, was transferred to the Texas Research and Engineering Institute in May 1981. The principal investigator, however, continued to be Professor C. Yaws. The chemical engineering research on the hydrochlorination reactor of the Silane Process, initially being carried out at MIT, was transferred in July 1981 to Solarelectronics, Inc.; the principal investigator continued to be Dr. J. Mui. Efforts to develop the FSR and the FBR for the Silane Process were supported by studies of the nucleation and growth of aerosol particles by Professor Flagan at the California Institute of Technology (Caltech) and the AeroChem Research Laboratories. Research continued on impurity effects at Westinghouse and by Professor Sah. There also were intensified studies for the development of the silane-FBR at both UCC and JPL.

In FY 82, the development contract with UCC was directed solely toward the experimental demonstration

of the engineering feasibility of silane-FBR technology. This program was conducted in collaboration with a complementary study in the JPL chemical engineering laboratory. Also, under Professor O. Levenspiel as principal investigator, a study of an alternative method for heating a FBR was initiated late in the year at Oregon State University. The effort was continued to fully characterize the conditions for the conversion efficiency and the kinetics of the hydrochlorination reactor for the Silane Process at Solarelectronics.

Further development of the SiH_2Cl_2 -CVD Process was underway in FY 82. Parametric studies were continued to describe the reactor designs and the operating conditions for the SiH_2Cl_2 synthesis and the silicon deposition steps. The objectives were to increase the conversion yields and the reaction rates of these steps. An economic analysis of this process was completed in July 1982 by the Texas Research and Engineering Institute under Professor C. Yaws.

The extensive, valuable study by the Westinghouse Research Center of the effects of impurities on the properties of silicon materials and on the performance of solar cells ended in February 1982. The conclusions derived, supported by measurements and studies in other laboratories, provided the basis for purity guidelines for FSA contracts and for efforts of private corporations to develop solar-grade polysilicon processes. A natural and important extension of this study to characterize silicon material requirements for very high-efficiency cells was proposed by Westinghouse and the Silicon Material Task in 1981. Unfortunately, this study could not be fitted into the FSA Project program.

In December 1983, the development of the SiH_2Cl_2 -CVD process was ended after the demonstration of the capability of high-conversion yields for the SiH_2Cl_2 preparation and silicon deposition reactors. HSC concluded that the flammability and explosion characteristics of SiH_2Cl_2 would force both the direct use of the SiH_2Cl_2 without storage and the remote location of the SiH_2Cl_2 preparation unit. There was no indication that HSC would use the SiH_2Cl_2 technology commercially.

In April 1983, after completion of the study to characterize the operating conditions of the hydrochlorination reactor for the Silane Process, the development of the silane-FBR and the investigation of the aerosol reactor by Caltech were the only efforts to remain in the Task program. A study was initiated in December 1983, and completed in December 1984, to model the silane-FBR system to provide a basis for interpreting the experimental data and for designing reactors and experimental plans. The experimental FBR effort at JPL ended in June 1985 with the achievement of having extensively characterized the operation of the silane-FBR system at high silane concentrations. Demonstration of the operation with the production of high-purity polysilicon product remained to be done. The experimental FBR effort at UCC ended in April 1986 with encouraging indications that long-term, steady-state operation was achievable. There had been only a partial demonstration of steady-state operation during extended periods, and the capability of producing high-purity silicon remained to be demonstrated.

SECTION III

Three Process Developments for Production of Semiconductor-Grade Silicon

A. DICHLOROSILANE CHEMICAL VAPOR DEPOSITION PROCESS

The two-step dichlorosilane (SiH_2Cl_2) CVD process was carried out by HSC under JPL Contract 955533. The first step, the generation of SiH_2Cl_2 , takes place in a reaction sequence patterned after the steps in the UCC silane process. As in the silane process, the processing sequence of the first stage consists of the following steps for the production of dichlorosilane:

- (1) SiHCl_3 is prepared by the hydrochlorination reaction of H_2 and silicon tetrachloride (SiCl_4) with metallurgical-grade silicon (mgSi) in a FBR.
- (2) Purification of SiHCl_3 by removal of metals as chlorides and of high-volatility gases.
- (3) Residual SiCl_4 is removed by distillation. The disproportionation reaction of SiHCl_3 into SiH_2Cl_2 and SiCl_4 takes place on a Dowex catalyst. The SiH_2Cl_2 is purified by distillation.

In the second stage, the high-temperature, H_2 -reduction of SiH_2Cl_2 deposits silicon onto heated filaments in a Siemens-type reactor (Figure 2). This process concept is based on the reasoning that, compared with SiHCl_3 , the use of SiH_2Cl_2 in a Siemens reactor would be advantageous because of its greater deposition rate, more favorable conversion yield per pass, and lower deposition temperature.

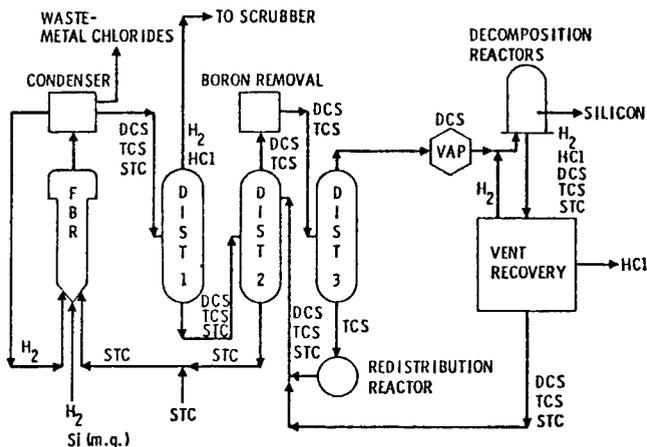
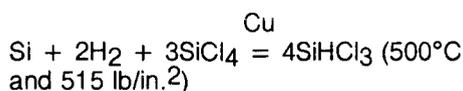


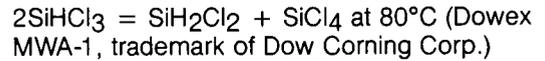
Figure 2. Hemlock Process Flow Diagram

The primary overall chemical reactions are:

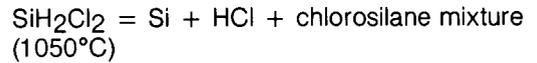
- (1) Hydrochlorination of mgSi:



- (2) Disproportionation reaction:



- (3) Silicon deposition reaction:



The SiCl_4 in the reaction product streams is recycled, as is the H_2 recovered from both the product stream of the hydrochlorination reactor and from the Siemens-type reactor. This recycling eliminates the need to deal with a large amount of SiCl_4 as a by-product. The greater deposition rate and yield characteristics, together with reactor improvements, also indicate a potential for a considerable decrease in reaction-energy use.

The program plan contained tasks to characterize the SiH_2Cl_2 deposition reaction, to demonstrate the scalability of the deposition reactor using an intermediate-sized unit, to study the SiHCl_3 to SiH_2Cl_2 redistribution reaction and the characteristics of Dowex catalysts, and to do a preliminary engineering design of an EPSSDU.

The conditions of flow rate, SiH_2Cl_2 concentration, and temperature were systematically varied in a study of the deposition reaction. Concurrently, experiments with the redistribution reactor provided information on the kinetics and catalyst behavior, such as transport properties, conversion efficiency, and catalyst lifetime. Optimal operating conditions were derived from the results. In a series of runs it was shown:

- (1) The redistribution reactor could be run 95% on line.
- (2) The intermediate-sized deposition reactor used about 90 kWh/kg and gave an average of 37 mol % yield with a deposition rate of 2 g/h-cm.
- (3) Because no vapor-phase nucleation occurred, there were no problems with fine powder formation.
- (4) The silicon produced was of semiconductor-grade purity.
- (5) The rod surface was acceptably dense and coherent. Solar cells from the produced silicon were made and tested by the Westinghouse Research Center. Their efficiencies, in the range of 12 to 14%, were as good as baseline cells prepared from silicon produced by the SiHCl_3 -Siemens process.

A major problem arose during the chemical and physical characterization of SiH_2Cl_2 . The SiH_2Cl_2 was found to have a very low and unpredictable ignition temperature, a broad flammability range, and an extreme tendency to detonate under confinement in air mixtures. To minimize these hazards, the process was redesigned with a provision to use H_2 to dilute the SiH_2Cl_2 immediately as it came out in the exit stream from the SiH_2Cl_2 distillation column. As a consequence, the HSC process does not include SiH_2Cl_2 storage.

The final phase of the contract firmly established the production capability of the SiH_2Cl_2 PDU as well as the throughput, yield, and energy-use advantages of using SiH_2Cl_2 in a CVD reactor. Based on a preliminary engineering process design, an economic analysis for a 1000 MT/year plant indicated a price of \$24/kg (in 1980 dollars) at 20% return on investment. There is no evidence the SiH_2Cl_2 CVD process has been installed in a commercial plant.

B. BROMOSILANE PROCESS

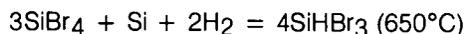
The feasibility of using a bromosilane chemical system for the production of polycrystalline silicon was examined by the J. C. Schumacher Co. under JPL Contract 954914. The apparent advantages of the SiHBr_3 system compared to the SiHCl_3 system were given as:

- (1) The capability to operate at lower temperatures without causing homogeneous nucleation and the formation of fine powders.
- (2) A decreased tendency for wall deposition and polymer formation.
- (3) An increased reaction rate for the H_2 reduction of bromosilanes.
- (4) Better partition coefficients for purification across the liquid-vapor phase boundary.

The recognizable disadvantage is the high raw material cost, but this would be greatly reduced in a closed-cycle process.

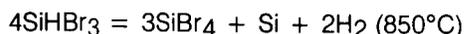
The primary overall chemical reactions are:

- (1) Generation of tribromosilane (SiHBr_3) from mgSi :

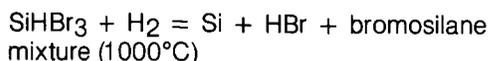


- (2) Silicon production:

- (a) Thermal decomposition:



- (b) H_2 reduction:



A major initial investigation dealt with the behavior of a high-velocity gas-phase reaction for the H_2 reduction of bromosilanes. After a chemical engineering analysis, a continuous-flow reactor was proposed into which silicon seed particles were introduced to be mixed with and conveyed by high-velocity gaseous reactants through the reaction zone. Early experiments, however, directed toward obtaining overall yield data and the full characterization of kinetics and thermodynamics of this reaction system, indicated the need for increased residence time and greater deposition substrate particle packing density. This led to a changeover to an FBR.

Limited experiments in the H_2 reduction of SiHBr_3 in a FBR gave a 60% yield at 1000°C. Analogous to the chlorosilane system, the major by-product is SiBr_4 . Analyses were performed of designs for processes incorporating a FBR for the deposition reactor and a hydrobromination reactor to generate the SiHBr_3 . These indicated that the Task goal could be reached using either hydrogen reduction or thermal decomposition of SiHBr_3 . Preliminary optimization calculations did now show distinct advantages for either path. Budget restrictions and Project schedule commitments forced termination of the work at this point.

Further development of this process at Schumacher was continued under private funding. A closed-loop bromosilane process analogous to the UCC chlorosilane process is projected. Composition measurements indicate a high-purity product from a 1-MT/year process development unit. The start-up of a 50-MT/year pilot plant and the planning for a 1000-MT/year plant have been announced.

C. SILANE PROCESS

1. Silane Production

The development of a process for the low-cost preparation of silane, for use as the feedstock for the production of low-cost semiconductor-grade polysilicon, was the basis for JPL Contract 954334 with UCC in October 1975. Advantages of silane as the intermediate for polysilicon deposition, compared to trichlorosilane (SiHCl_3) or silicon tetrachloride (SiCl_4), are a lower deposition-reaction temperature, a higher conversion efficiency, and lower environmental and corrosion problems.

Experimental evidence to support the concept had already been obtained by UCC in studies of the use of redistribution reactions catalyzed by a tertiary amine exchange resin to convert SiHCl_3 into dichlorosilane (SiH_2Cl_2), SiH_4 , and SiCl_4 . Indeed, the catalysis reaction was already being used by UCC for the commercial production of SiH_2Cl_2 from SiHCl_3 . A further advantage of the proposed redistribution reaction route was the separation of the gaseous products of the redistribution reactions that could be readily achieved by distillation. Using extant experimental data for the preparations of SiHCl_3 and SiH_2Cl_2 , coupled with a logical extension of these results to the production of silane, a preliminary

estimate of \$4.42/kg silane was given in the proposal for the manufacturing cost of silane with a process feed-stock of metallurgical-grade silicon. A credit for the sale of the by-product SiCl_4 was included in the calculation. Another preliminary estimate of the manufacturing cost of the polysilicon product, assuming the use of a Siemens-type reactor for CVD deposition, yielded \$9.90/kg silicon (1975 dollars).

The Silane Process consists of two primary steps (Figure 3). In the first step, mgSi is transformed into extremely pure silane; in the second, the silane is thermally decomposed to yield silicon. The only chemicals introduced into the closed-loop system are the mgSi feedstock and some make-up chlorine in the form of SiCl_4 . The main by-products of the process steps for chemical conversion, purification of intermediates, and silicon deposition are H_2 and SiCl_4 . These are recycled. Metal impurities are removed as chlorides.

The processing sequence consists of the following steps:

- (1) Production of trichlorosilane (SiHCl_3) from the hydrochlorination reaction of H_2 and SiCl_4 with mgSi in a FBR.

- (2) Purification of the SiHCl_3 by the elimination of high-volatility gases and of metals as chlorides followed by the separation of the residual SiCl_4 (for recycling) by distillation.
- (3) Disproportionation of SiHCl_3 into dichlorosilane (SiH_2Cl_2) and SiCl_4 .
- (4) Purification of the SiH_2Cl_2 .
- (5) Disproportionation of SiH_2Cl_2 into SiH_4 and SiHCl_3 .
- (6) Purification of SiH_4 by distillation.
- (7) Thermal decomposition of SiH_4 to yield silicon.

The primary overall chemical reactions are:

- (1) Hydrochlorination of mgSi :

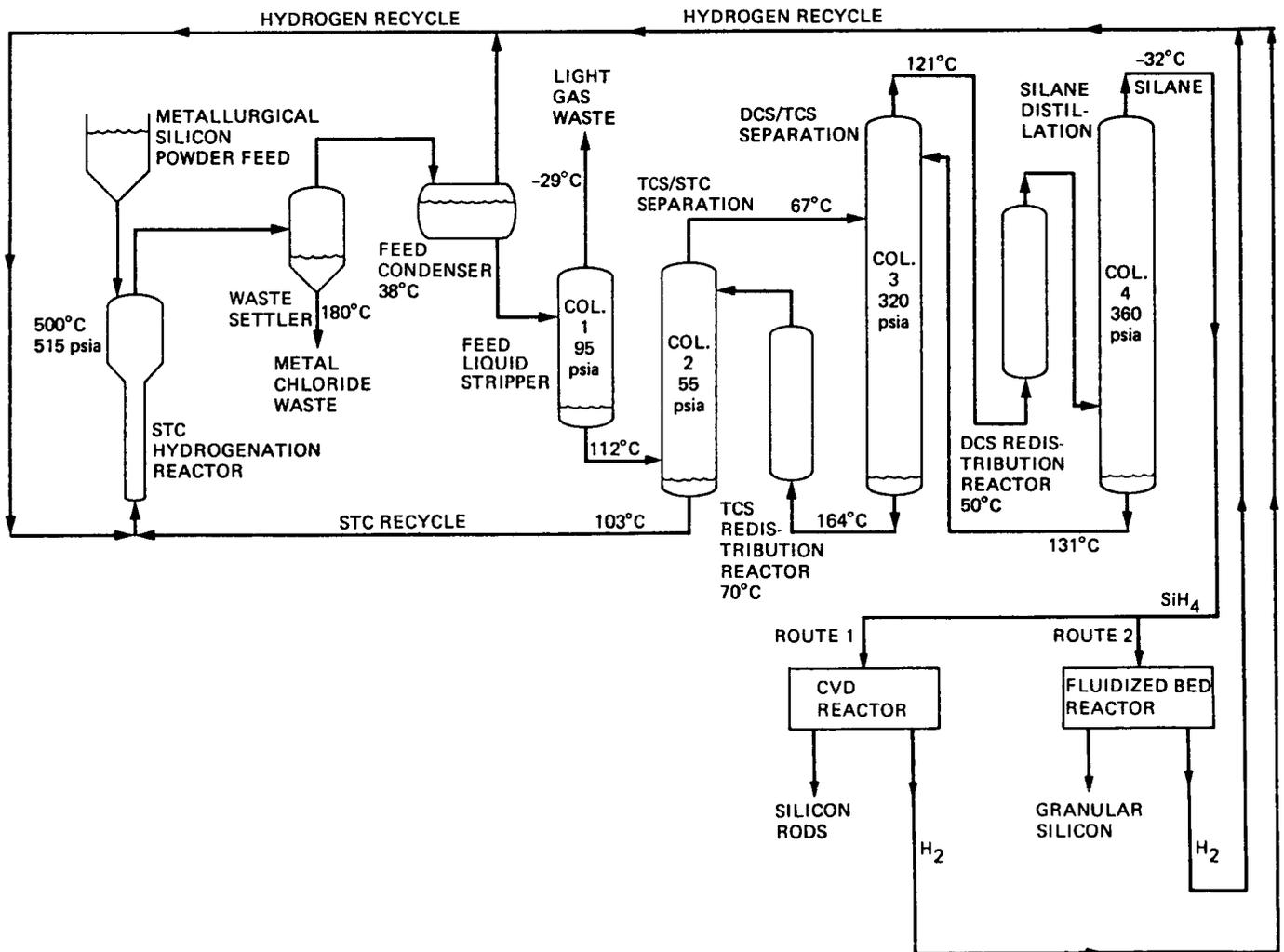
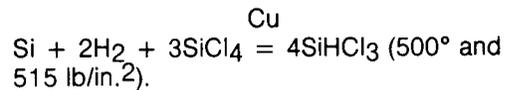
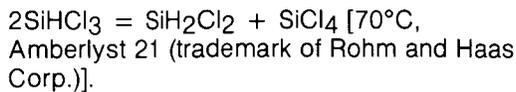
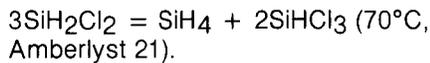


Figure 3. Union Carbide Process Flow Diagram

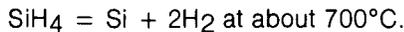
- (2) Disproportionation reaction 1:



- (3) Disproportionation reaction 2:



- (4) Thermal decomposition:



The SiCl_4 in the product streams from these reactions is recycled, as is the H_2 recovered from the silane decomposition and from the product stream of the hydrochlorination reactor. The initial statement of work consisted of the following tasks:

- (1) Experimental operation of a 10 lb/day mini-plant using a feedstock of varying mixtures of chlorosilanes. Equipment consisted of a redistribution reactor and one distillation column to produce silane.
- (2) Experimental operation of a silane maxi-plant of the same capacity that used the same feedstock, but consisted of two redistribution reactors and three distillation columns.
- (3) Process studies involving the experimental determination of the effects of redistribution reactor parameters, analyses of thermodynamic and kinetic characteristics, evaluations of purification methods, and development of procedures for silane storage.
- (4) Calculations based on experimental data to evaluate the economic and energy-use characteristics of an overall silane process.
- (5) Study of the reaction for the direct synthesis of SiH_2Cl_2 from metallurgical-grade silicon. This statement of work did not provide for development of a reactor to convert silane into silicon.

Engineering feasibility of the process was shown in Phase I of the contract by:

- (1) Experimental operation of a PDU to produce silane from a feedstock of chlorosilane mixtures.
- (2) Experimental characterization of the hydrogenation redistribution reactors.
- (3) Establishment of closed-cycle production of high-purity silane in a process coupling the hydrochlorination reactor to the PDU.

- (4) Obtaining extensive data for the reaction chemistry, kinetics, chemical properties, and thermodynamics to support the process development efforts.
- (5) Evaluating purification methods and developing procedures for silane storage.
- (6) Experimental characterization (begun in January 1977) of a FSR for the conversion of silane to submicron-size silicon particles and of the means for consolidating the powder.
- (7) Preliminary experimental study of FBR technology as an alternative silane-to-silicon conversion reactor. The technical feasibility of the part of the process for the production of silane from mgSi was confirmed in April 1978.

In October 1977, in response to the requirement by the DOE for an acceleration of the development schedule to enable the production of increasing quantities of polysilicon needed for the anticipated expansion of the PV solar cell industry, Phase II was begun to run concurrently with the Phase I studies. The main objectives were to provide an information base for experimental silane and polysilicon production facilities, to prepare a preliminary design for a 25-MT/year polysilicon production facility, and to carry out economic analyses for both the 25-MT/year experimental facility and for a 1000-MT/year commercial plant. A detailed design for a 25-MT/year facility was developed. Investment and operating cost data were calculated for both the 25-MT/year facility and the 1000-MT/year production plant.

Realizing that a 25-MT/year unit was probably impractically small and that increased production capacity would be more appropriate, JPL requested UCC to provide an engineering and cost analysis of a proposed 100-MT/year EPSDU. The EPSDU was defined as an experimentally integrated unit. It contained all of the experimental equipment, including units for conversion reactions, purification, separation, and recycling that were conceived as being required to investigate and characterize the complete process. The calculations and analyses led to the following conclusions:

- (1) Costs for capital equipment, operation, and maintenance labor were quite insensitive to size changes of the small facilities.
- (2) The 100-MT/year EPSDU would be more easily assembled because the 25-MT/year EPSDU would require some unconventional and, in some cases, less suitable equipment.
- (3) Some volume and sizing problems, which should be examined directly in this phase, might not be amenable to study in the 25-MT/year EPSDU. Thus, the scale-up factor for the equipment could be more readily and extensively investigated with the 100-MT/year EPSDU.

- (4) Data obtained for the operation characteristics of the 100-MT/year EPSDU, such as heat losses and waste disposal requirements, would be more applicable to the design of a large-scale plant.
- (5) Design arrangements of some equipment for the 100-MT/year EPSDU, such as distillation columns, would be expected to be similar to those for large production plants.
- (6) Increase in EPSDU size would not cause additional technical problems.
- (7) Site size would be about the same for the two EPSDUs. The conclusion was that the advantages of a 100-MT/year EPSDU warranted the small additional cost from \$4,000,000 to \$4,500,000.

The contractual effort preceding the EPSDU phase, involving a coordinated program of four UCC laboratories, had centered on the silane production section of the process and had resulted in establishing the technical feasibility of each of the reaction units. Experimental data of the physical properties of all of the chemical compounds involved in the reactions had been obtained as functions of ranges of operating conditions. Experimental data had been garnered for the reaction conditions both to characterize the reactions and to optimize the conditions for product yield, throughput rate, energy use, purity of product, and economics. Designs had been developed for chemical reactors and purification units. A process design had been performed to obtain a complete and technologically simple process flow sheet to be used as the basis for the design and costing of an EPSDU. An economic analysis had been done for the overall process. The results confirmed the expectations that the UCC process could meet the then LSSA Project objective, assuming that a suitable silane-to-silicon conversion reactor could be developed.

Favorable progress on the work elements of Phases I and II led to a Phase III for the detailed engineering of the design, fabrication, installation, and experimental operation of the EPSDU. Experimental studies were to examine parametric variations, to determine steady state operating conditions, to optimize the yield and operating efficiency of the overall process, to examine the requirements for instrumentation and controls, and to perform calculations and analyses of designs and economics. This information not only would provide the basis for the EPSDU design, but also would provide projections of operation characteristics and economics for a large-scale production plant.

The Phase III plan required that tasks were to be carried on concurrently for the continuation of experimental developments of the processes for the conversion of silane into silicon using FBR and FSR techniques and of the optimization of the operation of the hydrogenation reactor. Information and analyses from this work

would be introduced into the design, fabrication, and installation of the EPSDU at appropriate times. Also, investigations with the silane PDU would continue to explore operating parameters and secure information for iterations of unit designs. Other experiments, critiques, and economic analyses in support of the EPSDU phase would also be continued at JPL and under contracts with other laboratories and consultants.

A complex, detailed, work-breakdown structure (WBS) was used to describe, coordinate, and track the large number of EPSDU activities. The seven major categories of the WBS and further subdivisions for tasks and work items in these major categories are shown in Table 3. Work items were defined as the smallest, practical, work-subdivisions based on cost, duration, and schedule.

Using this control system, extensive effort for the design, specification, and fabrication and procurement of equipment was carefully managed. The initial WBS covering FY 80 (the 45-month EPSDU phase having begun in April 1979) was replaced by a revised WBS for FY 81, 82, and 83 to enable the increasingly complex interplay of activities to be more properly controlled. The revision not only emphasized a primary division of the EPSDU program into a section for silane production and a section for silicon production, but also showed a schedule extension from December 1982 to May 1983. The additional time was to provide, in part, for the development effort and design of the pyrolysis system.

Contributory experimental studies of the hydrogenation-reactor to obtain parametric data describing yield and rate efficiencies were performed by Dr. J. Mui under contracts with MIT and then Solarelectronics, Inc. Conducted concurrently with the EPSDU activities, these investigations yielded information that became the basis for the design calculations for this reactor.

The EPSDU program was affected severely by the sharp reduction in funding for the FSA Project in FY 81. As a consequence, a series of stop-work orders and work-statement revisions was issued starting in March 1981 in an effort to maintain an intact overall program with lower funding. These contract changes involved the pyrolysis/melting and the FBR work items. These attempts, however, were inadequate when the full impact of the budget cut-backs on the UCC EPSDU program was determined. It was concluded that the completion of the installation and the operation of the EPSDU were not possible under the new budget limitations.

At this time the EPSDU process design package had been completed. The EPSDU site had been prepared along with the installation of underground utilities, pre-engineered-type buildings, and the EPSDU structure. Most of the equipment had been procured and delivered and much of the major equipment had been installed in the gantry. Only the mechanical installation of piping, valves, and some units and the electrical work remained to be done for the EPSDU installation. The R&D effort for the fluidized-bed technology was also unfinished.

Table 3. EPSDU Work-Breakdown Structure

Silane Process (Union Carbide)

EPSDU: Design/Procurement
Process Design
Engineering Design
Equipment Specifications/Procurement
Installation Drawings
Environmental
Cost Estimate
EPSDU: Equipment Fabrication/Delivery
Mechanical
Electrical
Instruments and Controls
Other Equipment
EPSDU: Installation and Checkout
Site Evaluations
Installation
Checkout
EPSDU; Operation
Preparation
Start-up
Modification
Initial Feasibility Demonstration
Data Generation and Analysis
Silicon Consolidation R&D, 1986 LSA Goals
Off-Site Quality Control Analysis
Final Performance Run
Equipment Durability Assessment
Shutdown
Commercial Process Economic Analysis
Process Design
Engineering Design
Cost Estimating
Assessment and Reporting
Process Support R&D
Free-Space Reactor Development
Melting/Consolidation Development
Fluidized-Bed Reactor Development
Quality Control
Management And Deliverables
Project Management
Program Management
Deliverables

Attempting to devise a strategy to permit the completion of the UCC-EPSDU program, options were explored in a series of conferences involving UCC, JPL, and DOE. Motivation for these meetings was the consensus that every effort be made to devise a means of completing the EPSDU demonstration. Because information then available indicated DOE funding for FY 82 and FY 83 also would be severely inadequate, the EPSDU program could never be completed without a substantial financial contribution by

UCC. Discussions, therefore, centered on means of bringing about an agreement for UCC to cost-share the program.

The only mutually agreeable option enabling the achievement of the FSA objective was to transfer the title of the EPSDU equipment to UCC. In return, UCC would be obligated to complete the installation and check out, start up, and operate the EPSDU for at least 1 year. UCC also would supply a final report describing any modifications and the details of 1 year of operation. The EPSDU data for the silane-to-silicon conversion step would not be provided because a proprietary deposition reactor, licensed from Komatsu Electronic Materials, Inc., was to be used. Under this arrangement, UCC was required to pay for all costs involved in installation and operation, including costs of transferring the equipment to a different location. The FSA Project agreed to continue funding the development of the silane-FBR. A careful JPL analysis indicated that this arrangement would oblige UCC to spend in excess of \$6.4M in exchange for the title to equipment that cost \$2,765,655. The EPSDU transfer was authorized by JPL in September 1981. Under the contract, the equipment was transferred from East Chicago, Indiana, and installed in Washougal, Washington. All of the site preparation, plant construction, and EPSDU check-out, start-up, and operation were accomplished with UCC funds.

The EPSDU check-out began in July 1982 and was completed 1 month later (Figure 4). Concurrently, plant operation and safety manuals were written. Various equipment and design modifications were implemented during

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Figure 4. Silane Process EPSDU

the check-out, start-up, and operation stages. As the initial step in the start-up, the first SiHCl_3 was produced in November 1982, and the first high-purity silane and polysilicon, respectively, were produced in January and February of 1983. The average purity for the silane produced in February was $99.08\% \pm 0.64$ with $0.37\% \pm 0.25 \text{ H}_2$, $0.56\% \pm 0.37 \text{ N}_2$, and $0.12\% \pm .07 \text{ He}$. Concurrently, the polysilicon purity data obtained from the second run with pure silane were 0.021 ppb B, 0.119 ppb P, and a resistivity of 898 ohm-cm. The EPSDU presently is routinely producing very high-purity silane and polysilicon. A 1200-MT/year commercial plant, based on the design and operating experience of the EPSDU, has been installed at Moses Lake, Washington. It now is in operation producing very high-purity silane and polysilicon.

2. Silane-to-Silicon Conversion

The silane-to-silicon conversion reactors in the 120-MT/year EPSDU and in the 1200-MT/year commercial plant are chemical vapor deposition, Siemens-type reactors that were developed and patented by Komatsu Electronic Metals Ltd. The silane and silicon products of these installations are semiconductor grade or higher, and the overall production of each product is satisfactory. Although lower operating costs had been estimated for the silane-Komatsu reactor process, as compared to the costs of the conventional Siemens-trichlorosilane process, it was evident from the beginning of the development contract that a different, lower-cost, deposition reactor having higher throughput and lower energy use would be required to meet the polysilicon low-cost goal of the Project. The program to develop such a reactor was carried out in the laboratories of UCC and JPL. It involved investigations of the FSR and the FBR.

a. *Free-Space Deposition Reactor.* The first effort at UCC to develop a different deposition reactor began in January 1977 and centered on the FSR. In an FSR, chemical reactions take place in the gas phase away from any wall. The silane enters the FSR as an axisymmetric jet, expanding into the hot reaction zone. The gas velocity, the temperature profile, and the reactor geometry need to be controlled to prevent any silane from reacting at a wall and depositing silicon. Operating with a conversion efficiency $>99\%$, the experimental FSR yielded a product which was a mixture of silicon particles ranging in size from submicron to a few microns in diameter. The objectives of the UCC-FSR program were:

- (1) To demonstrate long-term operation capability.
- (2) To evaluate methods for consolidating the product.
- (3) To establish product purity.

Numerous models, developed by UCC and its consultant, provided insights for the design of the FSR and the experimental conditions that should be studied. A refined version was a two-dimensional axisymmetric model in which the reactor was treated as a turbulent,

confined jet. Heat transfer from the walls as well as the effects of the chemical reaction were taken into account. Descriptions were obtained of the fluid flow, heat transfer, and the spatial chemical reaction dependencies on the influences of the wall temperature, the silane mass throughput, and the reactor geometry. Predictions involving sharp changes in the flow direction and a high velocity toward the wall were used as evidence for the cause of powder build-up on the wall. Descriptions of the nature of the heat flow and gas velocity were believed to show that the model was suitable for use in scaling up and modifying the reactor design. Despite some success in fitting experimental data to the model, the model was not established experimentally. Also, until the phenomena of particle formation was incorporated, the model could not be completely representative of the reactor system.

After additional data revealed that some simplifying assumptions were inappropriate, the model was refined further to take into account the profiles of nonuniform wall temperatures, injector positions, and varying properties of the gas. The resultant model was validated experimentally by its predictions of internal reactor temperatures, the dependence of silicon yield on silane flow rate, and the extent of wall deposition. Further correlations showed that the control of heat transfer from the wall was critical for long-term runs and indicated that silicon production of 100 MT/year could be reached with an 18-in.-diameter reactor.

Demonstration of long-term operation, with a goal of 2.3 kg/h for 24 h and determination of the maximum throughput capability were emphasized in the second phase of the FSR development by UCC. In two 24-h runs at silane flow rates $>2 \text{ kg/h}$, silane conversion yields $>99.6\%$ were reached without reactor plugging. The maximum throughput was found to be 4.5 kg/h based on 98% yield. Because of silicon deposition on the reactor wall, apparently caused both by insufficient heating and penetration of unreacted SiH_4 into the recirculated flow, a modified heating arrangement was necessary. It also was evident that product purity would require the use of a quartz liner.

In the next series of experiments, using a different temperature profile, hard wall deposits were eliminated and silicon conversion yields $>99.99\%$ were obtained. Despite attempts to control operating conditions to avoid wall deposition, the major reactor problem continued to be the build-up of powdery silicon on the walls. Use of a wall scraper to prevent the accumulation of thick deposits was partially successful. A second major problem, involving sharp decreases in particle size that resulted from the use of temperature profiles intended to eliminate wall deposition, presaged difficulties in maintaining purity and in transporting the particle product.

Conversion of the FSR-particles into silicon shot in a continuous melter-shotter unit was attempted by Kayex, under contract to UCC. Despite a favorable analytical prediction, the experimental operation was not successful. The powder melting was difficult, the melt time was

too long, and there was insufficient cooling time to prevent splattering in the collection vessel.

b. *Fluidized-Bed Deposition Reactor.* Although the FSR development was emphasized, an exploratory investigation of silane pyrolysis in an FBR was conducted during the period of January 1977 to March 1979 at UCC's Parma Research Center. The main objective was to determine the feasibility of producing dense, coherent coatings on seed particles while preventing the formation of submicron particles of silicon (dust). The FBR was an 8.5 cm inside diameter (ID) quartz tube. Several distributor-plate designs were examined in experiments operated during a temperature range to 1000°C. Conversion efficiencies were high at temperatures from 700 to 900°C, but only dense coatings were obtained above 950°C. Although the amount of dust formed at 7% silane seemed to be acceptable, excessive amounts occurred at about 23% and the reactor walls were coated with dense CVD coatings. Obviously, the reacting system was complex and undesirable products could be prevented only by defining and carefully controlling the temperature and the fluidization characteristics.

A very encouraging preliminary economic analysis for a 100 MT/year FBR unit indicated an annual operating cost of \$1.73/kg (1975 dollars) for the silane-to-silicon conversion. This gave a final product cost for polysilicon of \$8.48/kg (1975 dollars), taking into account the factors of a 15-year plant lifetime, 10-year depreciation, 48% federal income tax, 100% equity financing, 2-year construction time, and a 25% discounted cash flow (DCF) rate.

This exploratory study by UCC provided a preliminary description of the operating conditions required to obtain dense growth, to prevent plug formation that would shut down the FBR, and to minimize fine particle generation. Although the reasonably successful runs were made using low silane concentrations, the conditions and, thus, the feasibility for reactor operation at economically attractive concentrations of greater than 10%, remained to be established.

To obtain a design for product removal in a semi-continuous mode of operation, techniques for removing the larger particles from the FBR were investigated. Binary-size systems, containing large particles in a bed of fines and multidisperse systems in which there were wide size distributions of particles, were used in the experiments. A 1.5-in. ID fluidized pipe connected at the bottom of a 6-in. ID FBR was the primary separation method used. A suitable separation for the binary system was obtained for diameter ratios 2.55. Continuous separation occurred in the polydisperse system. The UCC results indicated that the conditions for product withdrawal needed to be carefully controlled for adequate separation.

The UCC experiments with a 6-in.-ID FBR began in April 1981 after a preliminary study of silane pyrolysis in a fixed bed. In a series of seven experiments, the capability of operation at silane concentrations up

to 21% was demonstrated without problems of agglomeration in the bed. Very small amounts of fine particles were formed, and the growth in the seed particles was dense. Mass-balance calculations showed that silane decomposition was essentially completed (99.7%) for silane concentrations up to 21%, under operating conditions of a bed temperature between 640 to 685°C and a bed height of 36 in. The temperature of the distributor plate was critical for long-term operation, because it rapidly became plugged if its temperature exceeded about 400°C. Although two 6-h runs were made, no attempts were made to approach steady-state operation by use of seed particle addition or product removal. The ability to heat the bed through the reactor walls without perceptible coating or wear also was shown in these short-time runs.

Based on this experience, several modifications of the reactor were made. The bed height was increased to 80 in., additional heating was provided, and the distributor plate was redesigned for direct cooling of the bottom surface. In 1982, a suitable operating window was defined for a steady-state condition. In a run covering 33 h of accumulated time, there was complete silane conversion. The capability for removing product silicon in batches and for adding seed particles was demonstrated. The critical operating parameter was the temperature distribution from the distributor plate to the top of the bed. The plate must be kept to about 300°C to prevent its clogging. A top-of-the-bed temperature of 750°C gave both good conversion and deposition results.

The 6 in. FBR was transferred from the EPSDU site in East Chicago, Indiana, and installed at Washougal, Washington, in August 1982. In three long duration runs in the last quarter of 1983, the total run time was 80 h with the longest single continuous run being nearly 45 h. Shutdown was voluntary. The overall seed particle mean diameter growth was from 300 to 500 μm with the maximum silane feed concentration being 24% in H_2 and the average feed rate of silane was 2 kg/h. Scanning electron microscope (SEM) and optical micrograph analyses indicated a dense 100-mm-thick deposition layer. Composition analyses showed, however, the presence of large amounts of the metals present in the Incoloy 800 H from which the reactor was fabricated. This severe contamination problem was analyzed in a critical review at JPL. The conclusion that the contamination was caused by abrasion of the reactor wall by silicon particles was derived from comparisons of similar occurrences in other FBR systems and from calculations using an abrasion model. The proposed solution was the insertion of high-purity quartz and polysilicon liners as barriers. Several long-term runs have been made using these liners. Operations went smoothly for a polysilicon liner in a run of 66 h and for a quartz liner with a total run time of 110 h. Although the amounts of impurities decreased, considerable improvement is still necessary for the production of semiconductor-grade silicon. Also, a common occurrence using a quartz liner is liner cracking during reactor cool-down. The economic practicability for use of a quartz liner must be demonstrated with data for an adequate throughput with an acceptable production time before cool-down.

The FSA-sponsored development of the silane-FBR ended in April 1986. UCC is continuing the program under corporate funding, seeking to demonstrate the following reactor attributes required for the low-cost Silane Process:

(1) Preparation and addition of suitably sized, pure seed particles.

(2) Steady-state operation with high throughput and withdrawal of product.

(3) Production of high-purity material.

The next step will be to verify FBR operation in the pilot plant. Ultimately, the FBR will be installed as the primary deposition reactor in large-scale, Silane Process production plants.

SECTION IV

Ten Process Developments for Production of Solar Cell-Grade Silicon

A. SYNTHESIS OF SILANE AND SILICON IN A NONEQUILIBRIUM PLASMA JET

The original objective of this program, carried out by AeroChem Research Laboratories, Inc. under JPL Contract 954560, was to determine the feasibility of using a nonequilibrium plasma jet to prepare the high-volume, low-cost, high-purity silane or solar cell-grade silicon from chlorosilanes and H₂. Near the end of the program, the emphasis on this method was changed to determine the feasibility of preparing amorphous silicon films directly for PV devices. The nonequilibrium plasma jet is produced by partially dissociating H₂ to hydrogen atoms in a 50-torr to 100-torr glow discharge and then expanding the H/H₂ mixture through a nozzle. This produces a high flux density of hydrogen atoms at concentrations of about 3 mol % with about 30% energy-utilization efficiency. The jet then is mixed with SiCl₄, and the reaction proceeds at temperatures of 400 to 600 K.

Suggested reaction paths were:

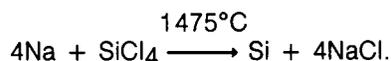
- (1) SiCl₄ + H = SiCl₃ + HCl.
- (2) SiCl₃ + H = SiCl₂ + HCl.
- (3) SiCl₂ + H₂ = SiH₂Cl₂.
- (4) SiCl₂H₂ + H = SiClH₂ + HCl.
- (5) SiClH₂ + H = SiH₂ + HCl.
- (6) SiH₂ + H₂ = SiH₄.

Yields of SiH₄, SiHCl₃, or SiH₂Cl₂ were found to be too low, however, to be economically attractive. Both amorphous and polycrystalline silicon films that adhered strongly to Pyrex, Vycor, aluminum, or carbon were prepared with either SiCl₄ or SiHCl₃ reactants. Using silane, strongly adhering films were more difficult to prepare. Doping such films with phosphorus by adding phosphine reduced their electrical resistivity by two orders of magnitude. It was concluded that the nonequilibrium plasma jet should be evaluated further as a highly efficient technique for producing amorphous silicon films for PV cells. Because of a Project program decision, however, no R&D program for this purpose ensued.

B. SILICON HALIDE-ALKALI METAL FLAMES AS A SOURCE OF SOLAR CELL-GRADE SILICON

The feasibility of using continuous, high-temperature, flame reactions of alkali metals and silicon halides to produce solar-grade silicon was investigated by

AeroChem Research Laboratories, Inc. Equilibria calculations showed ranges of operating conditions in which silicon can be produced in a condensed phase, with the alkali-metal salt byproduct as a vapor. The vapor-phase reaction of sodium (Na) with SiCl₄ was proposed as the primary step of a process.



Low-pressure experiments demonstrated that free silicon was produced. These experiments provided experience for the construction of reactant-vapor generators. Further experiments at higher reactant flow rates, with the coaxial injection of reagents, were performed in a low-temperature, flow-tube configuration. Relatively pure silicon was produced. A high-temperature graphite flow tube was built and continuous separation of silicon from NaCl was demonstrated. The conclusions of this study were:

- (1) Reactions of gaseous sodium (Na) or potassium (K) with SiCl₄ or SiHCl₃ produce stable high-temperature flames characterized by rapid kinetics and yield free silicon.
- (2) Flames of gaseous Na or K with silicon tetrafluoride (SiF₄) are characterized by much lower temperatures and slower kinetics. Free silicon is produced only if the reactor is hotter than about 1000 K. This prevents the formation of sodium fluosilicate (Na₂SiF₆). Additional heat input would be necessary to separate the product silicon from the sodium fluoride (NaF) in the gaseous phase.
- (3) Silicon produced from the Na/SiCl₄ reaction can be separated from the byproduct NaCl(g) if the reactor temperature is above 1750 K and the inert gas (argon) in the system is kept to a minimum.
- (4) Heat-release measurements showed the Na/SiCl₄ reaction to be mixing-limited, thus allowing a well-stirred reactor to be compact in volume.
- (5) Na-graphite compounds form at T < 1200 K causing severe material problems. Similar problems are observed with pyrolytic graphite or coated graphite. At T > 1700 K, these problems are not observed for graphite, although the coatings still fail.

It was recommended that the Na-SiCl₄ reaction system should be evaluated further as a process for producing solar-grade silicon.

C. SODIUM REDUCTION OF SILICON TETRACHLORIDE IN AN IMPACTION REACTOR

The feasibility of using continuous high-temperature flames of the rapid, exothermic reaction of Na with SiCl₄ to produce low-cost, solar-grade silicon was investigated further. Studies were performed by AeroChem Research Laboratories, Inc. under JPL Contract 955491 to obtain product separation, to test reactor and collector designs, to demonstrate continuous reaction-run capability, to measure heat-release parameters for scaling purposes, to determine the effects of the reactants and products on materials on reactor construction, and to make preliminary engineering and economic analyses of a scaled-up process. An impaction technique was used for silicon collection, and the feasibility of making and collecting silicon was demonstrated. In the final 1-h runs, silicon ingots weighing about 250 g were routinely produced, with separation collection efficiencies of about 80%. The longest runs of 1-1/2 h were limited by reactant reservoir capacity and not by design or equipment problems. Metal impurity levels were in the 1 to 10 ppm range or lower. There were no efforts to determine the optimum reaction conditions or the reactor design for conversion yield and product purity. Graphite for the reactor, and graphite coated with silicon, alumina, or silicon carbide for the collector, were shown to be satisfactory construction materials.

A preliminary process design (Figure 5) for a 1000-MT/year plant led to a calculation of a silicon-product cost estimate of about \$10/kg (1980 dollars). However, a Project program decision, forced by budget considerations, terminated research on this process.

Development of this process was continued at AeroChem under private funding. The research dealt

with gas-phase equilibria and reactor design, product purity, yield and throughput, and an economic analysis. The facility operated to produce 1.5 kg silicon/h, solving the three problems of handling Na gas, of materials and design for feeding the reactants into the high-temperature reactor, and of silicon removal. The yields were about 90% and this value should be improved in a large facility. The theoretical yield is 99%. The market price of the produced silicon was calculated to be \$17/kg (1982 dollars), where the cost of the raw materials amounts to 65% of the total cost. AeroChem is continuing this development.

D. ZINC REDUCTION OF SILICON TETRACHLORIDE

Thermodynamic and chemical engineering analyses of several processes for the preparation of silicon were performed as the first step of this program carried out by Battelle Columbus Laboratories, Ohio, under JPL Contract 954339. The processes included the zinc (Zn) reduction of SiCl₄ in an FBR to yield a granular silicon product, and several versions of the thermal decomposition or H₂ reduction of silicon tetraiodide (SiI₄). The Zn-SiCl₄ reaction was the only process capable of achieving the Task goal.

The primary chemical reactions for this process (Figure 6) are:

- (1) Silicon production:



- (2) Zn regeneration:

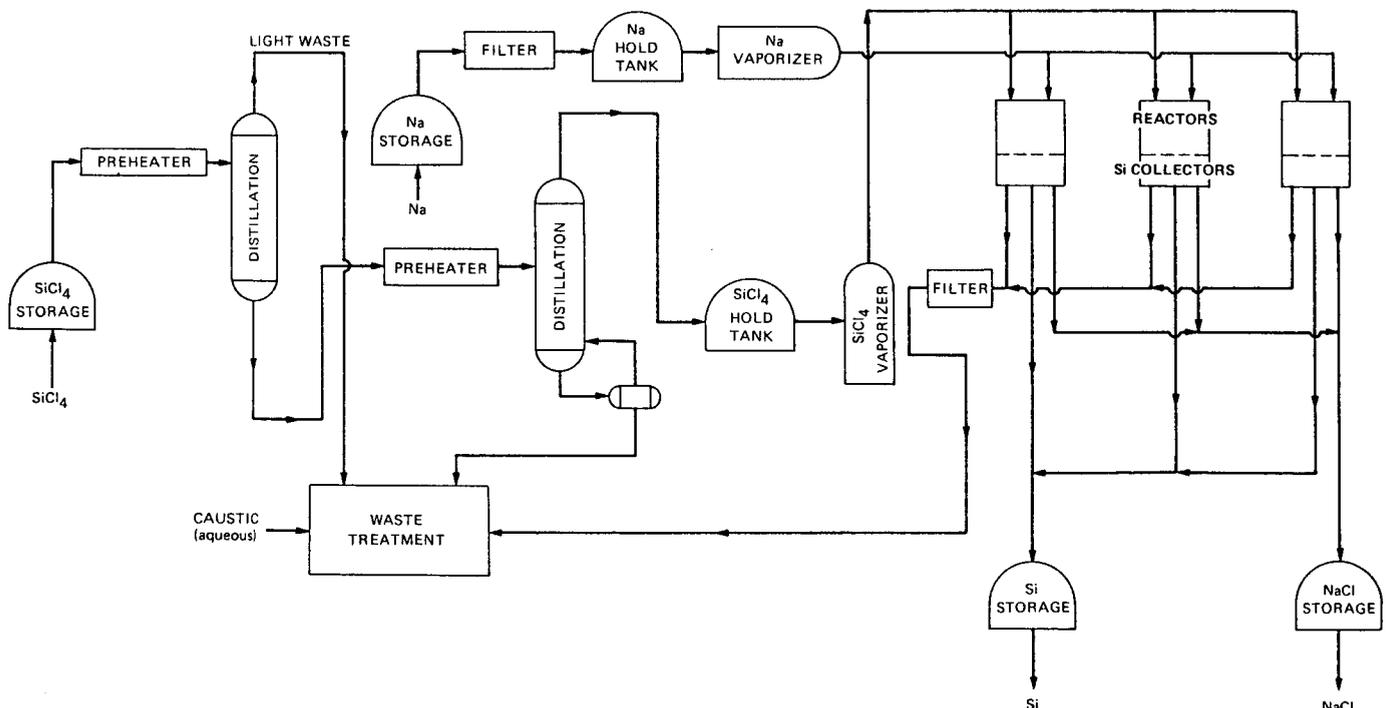
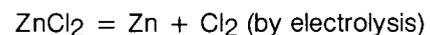


Figure 5. Aerochem Process Flow Diagram

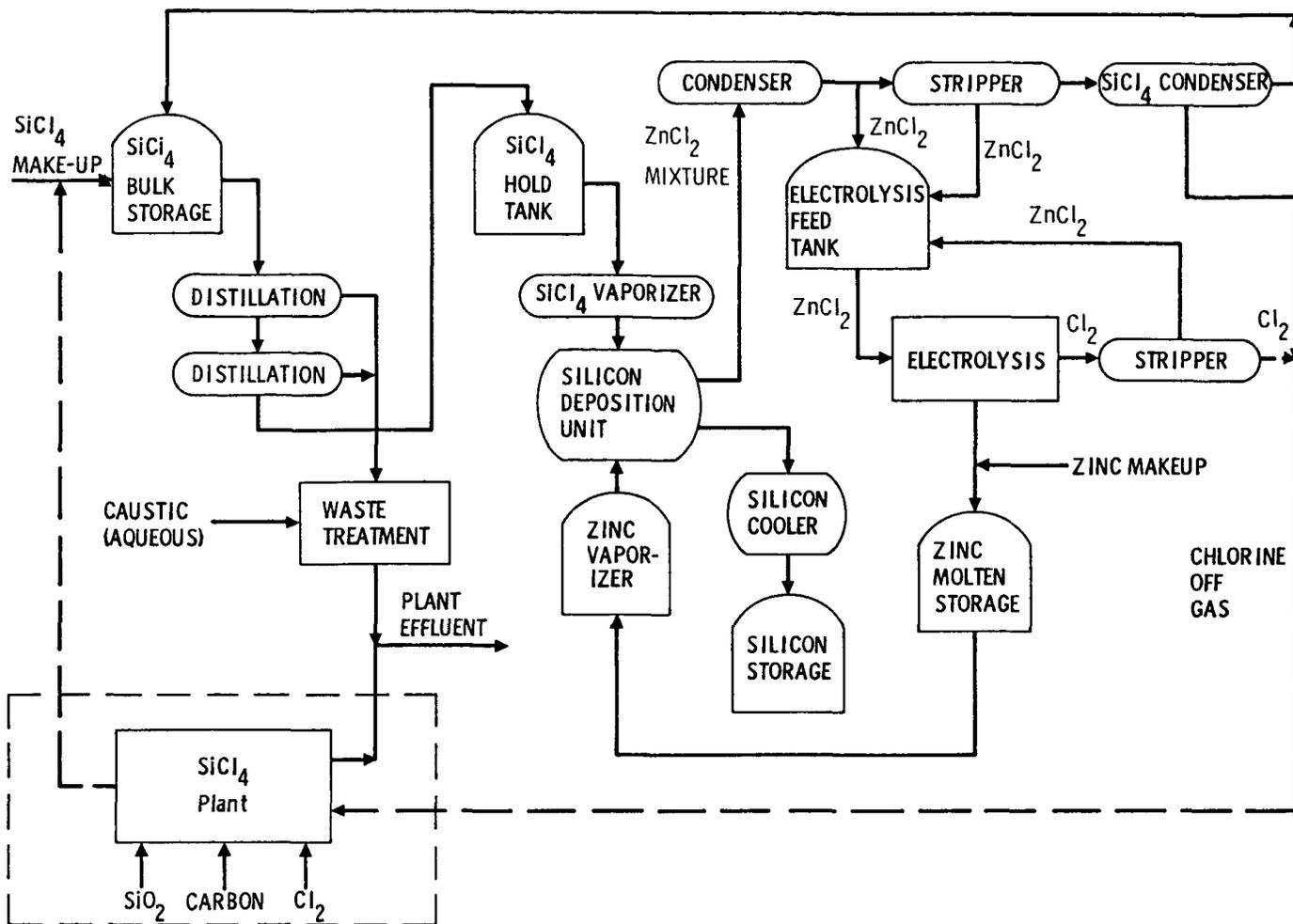


Figure 6. Battelle Process Flow Diagram

The first-phase experimental efforts dealt with the conditions and characteristics of the above two reactions.

A mini-plant, consisting of a 5-cm-diameter FBR and associated equipment, was used to study the deposition parameters of temperature, reactant composition, seed particle size, bed depth, reactant throughput, and methods of reactant introduction. It was confirmed that the permissible range of fluidized-bed temperatures was limited at the lower end by Zn condensation (918°C) and at the higher end by the rapidly decreasing conversion efficiency involving a change of 0.1%/°C from a 72% thermodynamic value at 927°C for a stoichiometric mixture. Use of a graded bed temperature increased the conversion efficiency compared to that obtained in an isothermal bed. Other aspects of the process, including the condensation and fused-salt electrolysis of the ZnCl₂ byproduct for recycling of Zn and Cl₂, were studied to provide information required for the design of a 50 MT/year experimental facility. This was visualized as the next stage of development. The purity of the product was determined in an ancillary study in which the granular product silicon was treated thermally by the Westinghouse Research Center to remove resid-

ual Zn. Solar cells made from resultant material had an average efficiency of about 12%.

As a phase of a program to establish the engineering feasibility of the process, a PDU was designed and installed. It was sized at 50 MT/year and consisted of four major units of the process (Zn vaporizer, ZnCl₂ condenser, FBR, and ZnCl₂ electrolysis cell). A series of operating and design problems was encountered in attempts to perform experiments with this integrated unit. Because of these experiments, improvements in the design and operation of these units were undertaken and their experimental limitations were partially established. Because more extensive redesigns of the equipment were prevented by budget restrictions, the performance characteristics of the PDU were not determined.

Projected silicon costs were calculated of \$10.29 and \$12.19/kg (1980 dollars) for a 1000-MT/year facility. The range depended upon the number and size of the FBRs and ZnCl₂ electrolytic cells used.

The development of this process was terminated before the operation of the PDU could be demonstrated.

E. DIRECT-ARC FURNACE PROCESS

Development of this two-step process for the preparation of solar-grade silicon was conducted by Dow Corning Corp., under JPL Contract 954559. The first step, the carbothermic reduction of quartz in a direct-arc furnace, is the basis of the commercial process for producing metallurgical-grade silicon. In this effort, the concept was to use extremely pure quartz and carbon reductants and to control carefully the conditions of the furnace. The second step, a unidirectional solidification procedure, resembled the Czochralski (Cz) technique for the preparation of single-crystal ingots. Thus, a considerable degree of purification would take place because of rejection into the liquid phase of impurities having very small, near-equilibrium, liquid-solid distribution coefficients.

An intensive survey of materials usable as reactants was made with the criteria being price, chemical activity, and purity. The purest quartz available in the United States and Canada was used in the experiments. The purest carbon reductant was found to be carbon-black-sucrose pellets. Test runs were performed in a specially-constructed, small-scale research 200 kVa furnace in which 100-kg quantities of silicon were prepared in 60-h runs at a maximum rate of 3 kg/h.

Impurity concentrations in the products, measured by emission spectroscopy, were found to be less than 10 parts per million by weight (ppmw) for each of the elements measured. Only aluminum (Al) and iron (Fe) were in the range of 50 to 100 ppmw. Attempts to attain further purification by vacuum evaporation were unsuccessful. The second-step purification by Cz crystal growth gave silicon with impurity concentrations below the limits established for this contract with the exception of Al (1 ppm), B (7 ppm), and P (0.5 ppm).

The inability to achieve the concentration goals set for both B and P was the most formidable barrier for this process. These goals were based on the objective of obtaining economically acceptable yields of single-crystal ingots by the Cz technique that were within specified resistivity limits. Thus, the process was finally effectively judged by the concentrations it yielded of B and P.

A product cost of \$12/kg (1980 dollars) was estimated for a 3000 MT/year plant. Further process development was recommended by Dow Corning, based on the degree of technical success achieved under the contract, the estimated product cost, and the consideration that a large part of the technology for the commercial plant could be applied to a scale-up of the modified process. This program was terminated, however, caused by both an inability to reach all of the concentration goals and to Task budget restrictions.

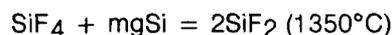
The development of this carbothermic process was continued under private funding by Solarex, Exxon-Elkem, and then by Elkem. The refining of metallurgical-grade silicon, using metallurgical processes, also is being pursued by other companies. At

Elkem, the carbothermic process has been carried further with considerable emphasis being placed on intermediate purification steps of leaching and remelting. Elkem is continuing this development based upon its projection that large-scale production will result in a cost only a few times that of mgSi.

F. SILICON DIFLUORIDE TRANSPORT PROCESS

This contract, carried out by Motorola Inc. under JPL Contract 954442, was for the development of a process in which the primary step is a temperature-gradient purification reaction. By reaction with silicon tetrafluoride (SiF_4), mgSi feedstock is converted into the intermediate silicon difluoride (SiF_2). In subsequent process steps the SiF_2 becomes polymerized and the polymer is converted into gaseous homologues of SiF_2 . These compounds then are disproportionated on a silicon particle bed to deposit silicon and regenerate SiF_4 , which is recycled (Figure 7). The overall chemical reactions are:

- (1) Formation of intermediate:



- (2) Polymer formation:



- (3) Silicon production:



Separate studies were devoted to each step of the process. An overall efficiency for silicon purification was calculated to be 53%, and the SiF_4 recovery was 95%. The separate reactions were characterized for yields and rates as functions of operating conditions, especially temperatures. Mass-balance data were obtained from gaseous phase and solid-phase analyses. Preliminary chemical engineering calculations were used to determine the relationships of reactor conditions, residence times, and conversion efficiencies. Composition analyses were determined by spark-source mass spectroscopy. A method of comparing the data for the product silicon with data for semiconductor-grade silicon was the basis for characterizing purity. The results, however, were ambiguous. Resistivity measurements indicated the need for further removal of electrically active impurities.

The chemical engineering, design, and costing for a 1 kg/h mini-plant were conducted in collaboration with Rafael Katzen Associates International, Inc. as consultants. A conceptual design was developed for a 100-MT/year plant in which the estimated capital cost was about \$6M. An economic analysis yielded a product cost of \$7.71/kg (1975 dollars).

This program was not continued through a demonstration phase that used the mini-plant. The decision to terminate was based on a technical evaluation.

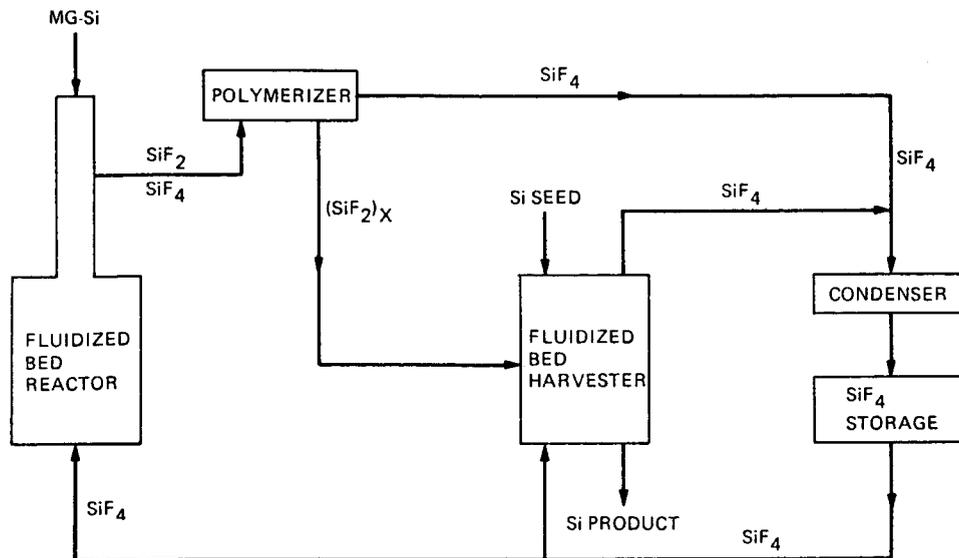


Figure 7. Motorola Process Flow Diagram

G. SODIUM REDUCTION OF SILICON TETRAFLUORIDE

This program, conducted by SRI International, Inc. under JPL Contract 954471, was intended to develop a process based on the reduction of SiF_4 by Na (Figure 8). The silicon-containing raw material was hydrofluosilicic acid (H_2SiF_6), a waste product of the fertilizer industry. In the process, H_2SiF_6 is converted into sodium fluosilicate (Na_2SiF_6). The latter is decomposed thermally to yield SiF_4 . Most of the development effort dealt with the reduction reaction, centering on studies of the reaction kinetics, the conversion yield, product separation, and purification techniques. The largest reactor used for the chemistry studies was capable of producing 1.4 kg of silicon in about 3 h. Experimental results indicated that: (1) the precursor formation reactions proceeded with good yields; (2) no problems in scaling up were predicted; (3) the reduction reaction could be controlled by SiF_4 pressure, Na particle size, and reactant concentrations; and (4) a liquid-liquid separation from NaF and other impurities was usable as a first step in product purification. The second purification step would be the use of a directional solidification technique.

Several process variables that affect the rate of reaction and the product yield were studied to determine the basis for a scale-up design. The size and geometry of the reactor, the temperature, and the Na addition method and rate were considered. Experimental results indicated a modified Na delivery system would be needed, that the silicon product purity would be controlled by the Na purity, and that heat dissipation would become more critical with increasing equipment size. In these experiments, the silicon product was recovered from the by-product NaF by melt separation and also by leaching. Composition analyses led to the conclusion that a solar-grade silicon was attainable by a unidirectional solidification. Only the concentrations of B and Al would be near the critical values.

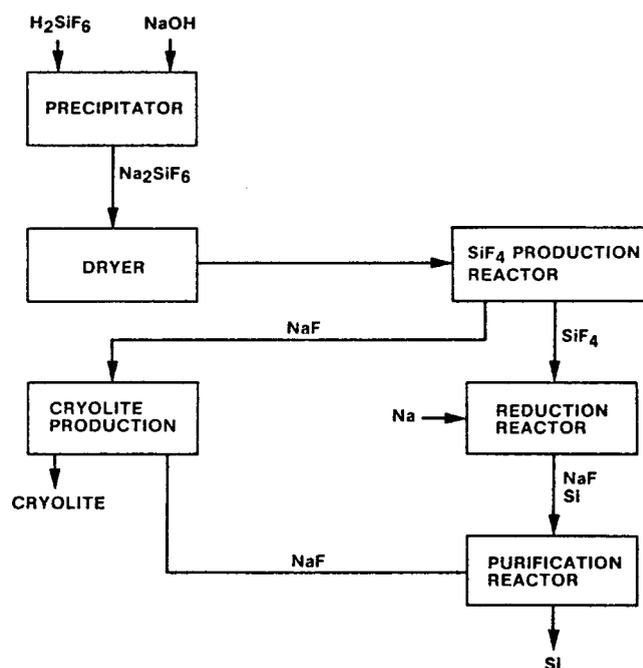


Figure 8. SRI International Process Flow Diagram

The conclusions were that the use of carefully purified Na and modifications of the reaction process would lead to further decreases in contamination.

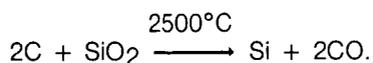
This program was terminated based on a technical decision. The chemical engineering design of a second stage apparatus and additional chemical engineering studies for the further characterization of this process were not done.

The development of this process continued at SRI under private funding. Leaching and melting methods are being used for silicon purification. Considerable progress was made in removing residual Na and other

impurities from the product silicon. Data from chemical analyses, wafer, and solar cell efficiency measurements have been used to demonstrate the high product purity. An average production rate of about 0.5 kg silicon/h was reached. This development is being continued at SRI International.

H. CARBOTHERMIC REDUCTION OF SILICON DIOXIDE

The feasibility of using a reactor with a plasma heat source for the carbothermic reduction of low-impurity silica to produce low-cost solar-grade silicon was investigated by Texas Instruments, Inc. under JPL Contract 954412. The proposed overall reaction was:



A computer-aided thermodynamic analysis was carried out using iterative free-energy minimizations. Optimum conditions for the reduction reaction were found to be a temperature range of 2500 to 3000 K for a reaction system consisting of silica and carbon black, with the reductant about 2% in excess. A computer simulation of the molecular dynamics was used to generate data on the formation of silicon as a condensate from a high-temperature plasma at various quench rates. The data indicated a maximum in the yield of silicon, but the required quench rate was beyond the experimental values and seemed to be too fast to be practical. In reaction studies, using a laboratory-scale experimental reactor, the maximum amount of silicon found in the sintered condensate product was 33%. The impurity levels in this product were reduced 10- to 100-fold from those present in the starting materials. A temperature gradient of 600 to 1500 K was mapped in the plasma flame. The results indicated a highly inefficient energy use because of poor heat transfer characteristics of the plasma flame. These results, and the low recoverable yields of silicon, were evidence of an unacceptable process and the contract was ended.

I. ROTARY CHAMBER REACTOR FOR USE IN A CLOSED-CYCLE PROCESS

This program, investigated by Texas Instruments, Inc., under JPL Contract 955006, was intended to develop a closed-cycle process for low-cost solar silicon using a rotary chamber reactor. SiHCl_3 generated in a hydrochlorination reactor was to be thermally decomposed. Laboratory-sized hydrochlorination and rotary-drum reactors were designed and fabricated. Preliminary experiments confirmed a capability for a high yield of SiHCl_3 . Up to 98% of the theoretical value was obtained. A preliminary analysis of the process cost based on this concept and using conservative capital cost estimates gave a value of \$7/kg (1980 dollars, without profit). The program was terminated because of budget restrictions.

J. HIGH-CAPACITY ARC-HEATER PROCESS

This program was conducted by Westinghouse Electric Corp. under JPL Contract 954589. It involved the development of a process (Figure 9) using existing electric arc-heater technology to generate high system temperatures for the reduction of SiCl_4 by Na and for the separation of the products. Completed as Phase I were the demonstration of feasibility, an engineering analysis of the process, and the design of a test system to verify the reaction experimentally. The second phase consisted of a detailed engineering analysis, the installation of an experimental system, and the determination of the operating characteristics.

As a first task, thermodynamic yields as well as the material and energy requirements for high-temperature multicomponent-multiphase systems were calculated using a computer program based upon equilibrium constants and free-energy minimization. The reductant candidates were H_2 , Na, magnesium (Mg), and Zn. Results of the calculations led to the selection of Na as the reductant. A similar set of calculations was used to determine the maximum concentrations of impurities possible in a molten-silicon product at the operating conditions of the reactor.

The reduction reaction, characterized in small-scale laboratory apparatus under conditions approaching those planned for the process verification testing (a temperature of 3000 K), led to the following conclusions:

- (1) A controlled reaction proceeds as predicted from the thermodynamic calculations.
- (2) Silicon can be separated and collected on a wall at a temperature above the dew point of NaCl.
- (3) The condensation rate essentially is predicted from the model calculations.
- (4) Larger collection rates should be obtained in a large-scale reactor because of increased heat and mass transfer to the wall.

The model used for these comparisons was the one developed for a large-scale system. Concurrently, the nozzles for the introduction of the reactants in liquid aerosol form were tested and characterized. Both atomized Na injection, using a sonic gas, and a novel peripheral SiCl_4 injection feed, were shown to be suitable.

Separation of the by-product NaCl as a gas and the collection of the silicon product were crucial to the success of this process. Two techniques for product collection had been proposed by Westinghouse. In one technique, the silicon nuclei and droplets could be collected on high-purity seed material injected into the reactor at a position following the chemical reaction zone. This method was not favored because it introduced additional problems involved in the preparation of the seed and in accounting for the competitive action of the homogeneous gas-phase nucleation. The preferred technique was a low-temperature treatment followed by

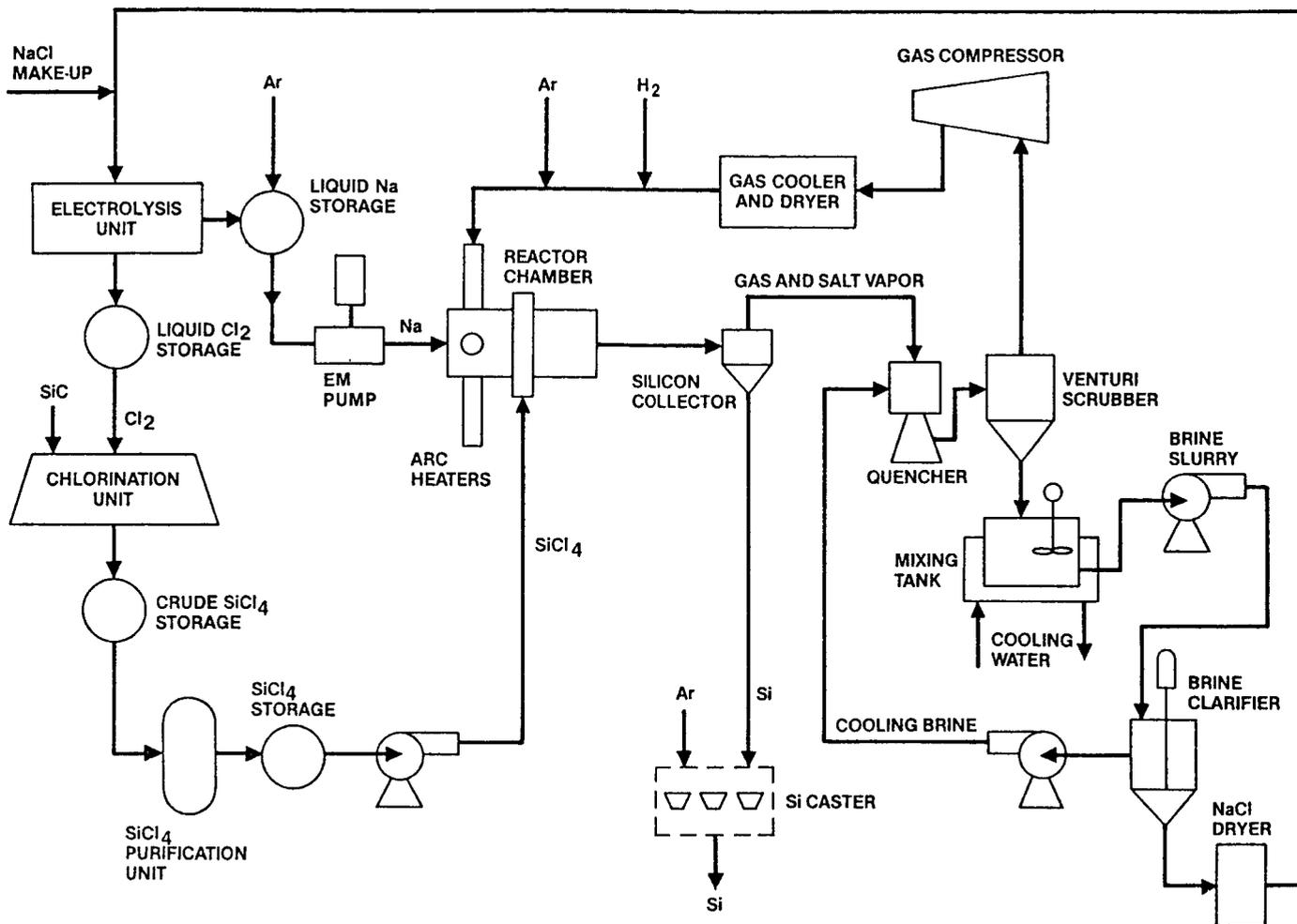


Figure 9. Westinghouse Process Flow Diagram

a high-temperature treatment. Silicon droplets were formed in a high-temperature zone following the comparatively low-temperature reaction zone. The final collected silicon product is the result of the agglomeration of the droplets. Reaction and thermal analyses by Westinghouse indicated the Na-SiCl₄ reaction was limited by inadequate mixing, the Na conversion was limited to about 10% because of a rapid temperature increase, and pure molten silicon droplets could be obtained in a small reactor length.

In February 1978, a 2-day critical review was held to examine the proposed mechanism for the process and the conclusions of Westinghouse. Attendees were Professors T. Fitzgerald (now at TRW, then at Oregon State University), S. Friedlander (now at University of California at Los Angeles, then at Caltech), O. Levenspiel (Oregon State University), B. Liu (University of Minnesota), and C. Yaws (Lamar University). Also present were Dr. D. Roberts (now at SRI International, then at Caltech), Dr. R. Gould (now at Universal Silicon Company, then at AeroChem Research Laboratories), D. Ciliberti, M. Fey, Dr. F. Harvey, E. Kothman, and Dr. T. Meyer (Westinghouse), and A. Briglio, Dr. R. Lutwack, and Dr. A. Praturi (JPL). The review concentrated its discussions on the chemical and physical

phenomena involved in the Arc-Heater Process and on the suitability of the various methods for the collection of a pure silicon product.

An analysis of silicon collection by seeding was done by the Caltech consultants. The recommendation that use of seeding was impractical was based on three major conclusions:

- (1) The method would fail for large, initial saturation ratios because of the rapid growth of small particles which are ineffectively collected.
- (2) The method would succeed if homogeneous nucleation could be suppressed, but the operable temperature range is very small.
- (3) The method becomes impossible if there are turbulent temperature fluctuations.

An analysis by the OSU consultants concurred. They added the statement that the calculated growth of the seed particles would be too small to be worthwhile, even with the assumption of successful operation in the optimum temperature region. The unanimously favored mode of collection was by condensation through thermophoretic transport to the reactor

wall. This solution was described by Professor Liu and was agreed to with some reservations by the other consultants. The problems of the effects of silicon fog were cited. The third collection mode considered was the growth of silicon on Na droplets, but this was considered to be a poor choice having several chemical and physical drawbacks.

The consensus of the review was that the silicon collection problem was serious, that the best solution might be difficult to define, that the optimum operating conditions might be hard to control, and that the implementation might be costly. Despite the inability to specify a clear-cut solution to the problem, this colloquium achieved the intended goals of critical analyses of the problem and of its possible solutions.

The testing facility was sized with a reactor capable of silicon production of 45.36 kg/h. Shakedown tests revealed some design problems, which were corrected with equipment and control modifications. For example, the arc-heaters were modified to improve heat transfer. A maximum gas temperature of 4000 K was demonstrated.

A test run, aborted by shutdown set off by a flame-out condition of the waste burner, yielded silicon material (97 %) admixed with NaCl. The presence of the NaCl in the silicon was attributed to an insufficiently high wall temperature separation, causing the products to condense together in the stream. The run verified that the condensation technique for silicon collection on a silicon skull wall was usable and that the kinetics under these conditions gave an essentially complete reaction. The need for modifications in some of the equipment was determined from the engineering analysis of the short-lived run. The complete demonstration of practical silicon preparation and collection was not achieved. The ability to separate the products completely remains to be shown.

A preliminary economic analysis gave a product cost of about \$13/kg (1980 dollars) for a 3000-MT/year plant.

The program was terminated after the one run because of budget restrictions and a Project program decision.

SECTION V

Eight Supporting Programs for Silicon Material Process Developments

A. MODELS AND COMPUTER CODES TO DESCRIBE SILICON-FORMING REACTIONS IN FLOW REACTORS

Two very useful models and computer codes were developed by Aerochem Research Laboratories, Inc., under JPL Contract 954862, for studying and predicting the performance of high-temperature, two-phase flow reactors. An example of the type of process that can be studied using these codes was an analysis of the Westinghouse's system being developed for the high-capacity, arc-heater process involving the Na reduction of SiCl_4 .

CHEMPART was the first code developed. It is an axisymmetric, marching code that treats the two-phase flow with models that describe detailed gas-phase chemical kinetics, particle formation, and particle growth for complex systems. This code, based on the AeroChem Low-Altitude Plume Program (LAPP) code, can be used to describe flow reactors in which reactants mix, react, and form a particulate phase. Detailed radial gas-phase composition, temperature, velocity, and particle-size distribution profiles are computed. Deposition of heat, momentum, and mass (either particulate or vapor) on reactor walls also are described. The second code, a modified version of the GENMIX boundary layer code, is used to compute rates of heat, momentum, and mass transfer to the reactor walls. This code lacks the detailed chemical kinetics and particle-handling features of the CHEMPART code. It has the virtue, however, of running much more rapidly than CHEMPART, while treating the phenomena occurring in the boundary layer in more detail than can be afforded using CHEMPART.

These two codes were used to predict particle formation characteristics and wall collection efficiencies for SiCl_4/Na flow reactors. It was found that large input enthalpies (large H-atom inputs) are required to prevent silicon droplet formation. In the case of the Westinghouse reactor, enthalpy is supplied by introducing large quantities of arc-heated H_2 . However, large H_2 flows mean short transit times of gas through the reactor resulting in short times for wall collection of silicon. An important expected application of these codes will be their use in finding operation conditions where droplet formation may be minimized and high collection efficiencies may still be realized in reactors of the Westinghouse type.

Many types of systems can be treated and there are many options for using a computer code the size of CHEMPART. Neither code is fully tested in its current form. Fuller development of these codes can be achieved from modifications that would result from more extensive applications.

B. KINETICS AND MECHANISMS OF SILANE PYROLYSIS

The objective of this program carried out by Aerochem Research Laboratories, Inc., under JPL Contract 955491, was to characterize the kinetics and mechanism of the formation growth of silicon particles from the decomposition of silane at high temperatures. The need for this study became apparent early in the development of a reactor for the conversion of silane to silicon in the UCC silane process. It was recognized that considerable amounts of unusable fine particles of silicon, formed in gaseous-phase nucleation reactions, are produced under some conditions of the thermal decomposition reaction. Experiments were aimed at determining rates at which gaseous-phase species form silicon-particle precursors, the time required to produce particles, and the rate of growth of silicon seed particles injected into the decomposing silane environment.

A high-temperature, fast-flow reactor (HTFFR) was modified to study the decomposition of silane and the subsequent growth of particles. Particle growth measurements were made as functions of temperature (873 to 1473 K), pressure (50 to 550 torr), and residence time (0.5 to 30 ms). Optical diagnostics, consisting of infrared absorption and Mie oscillations of light scattering at 90 deg from helium-neon (He-Ne) or argon (Ar^+) lasers, were used to determine the apparent growth rates and absolute sizes of the particles. The extent of silane decomposition pressure was measured by infrared absorption spectroscopy. These measurements determined the particle concentrations corresponding to the particle growth measurements. Particles were collected in the HTFFR observation zone as a check on the optical measurements of the particle concentrations. The growth of seeded-silicon particles was studied in the complex environment involving pyrolysis reactions of silane: temperatures were 873, 1173, and 1473 K. Seeded particles were either a commercial 5- μm silicon powder or samples of the submicrometer powder product of the UCC FSR. Attempts to observe silicon atoms and the molecular species SiH , SiH_2 , and Si_2H_6 were unsuccessful.

Results of the HTFFR experiments are:

- (1) An initial growth of particles occurs in an induction period of about 1 to 2 ms at 1200 K, producing particles of less than 0.05 μm radius.
- (2) The bulk of particle growth occurs in 1 to 20 ms after the induction period, with the particles growing to about 1 μm or larger at 1200 K.

- (3) Calibration of the Mie oscillations by Mie theory calculations agrees well with the determination of particle size by SEM.
- (4) The particles have a highly monodisperse size distribution.
- (5) Particle concentrations decrease with increasing residence time.
- (6) Two kinetic processes, perhaps, are occurring at the higher range of temperatures (> 1173 K). This suggests that:
 - (a) There may be an optimum silane concentration above which further increases do not increase the growth rate proportionally.
 - (b) Increasing the silane concentration increases the particle concentration to a limiting value.
 - (c) Seeded particles grow faster with increasing temperature.

A model was presented to explain the growth of silicon in a decomposing silane environment.

C. FINE PARTICLE GROWTH IN A SILANE FREE-SPACE REACTOR

The FSR was the first apparatus investigated by UCC for the thermal decomposition of silane-to-silicon. Studies were extended theoretically and experimentally at JPL by Dr. H. Levin, using the constant flow pyrolyzer and silane-to-molten silicon reactors. The primary problem encountered was the difficulty in handling, transporting, and melting of the fine particle product of mean mass diameter in the range of tenths of a μm . Contamination, because of the large surface area, also was a major concern.

Research at Caltech by Professor R. C. Flagan, under Work Order 61515, was started in 1980. The program objectives were:

- (1) To describe the theory of formation and growth of particles in the silane system.
- (2) To develop a reactor and reaction conditions for the growth of particles large enough to serve either as seeds for a silane-FBR or as a material suitable for direct melting.

In the first phase of the research, the theory of nucleation quenching by aerosol particles was extended, and conditions for growing larger particles were described. Design of a small, two-stage aerosol reactor was based on the theoretical analysis. A first stage generated the particles by homogeneous nucleation and a second stage controlled the conditions of silane concentration, temperature, and gas velocity to accentuate particle growth while inhibiting the formation of new particles.

Using 1 and 2% silane, particles smaller than $0.5 \mu\text{m}$ were grown to particles having a mean mass diameter of $6.2 \mu\text{m}$, and to $9.2 \mu\text{m}$, respectively. Electron microscope examination showed the few particles of $> 38 \mu\text{m}$ in diameter to have a fine structure, suggesting that this growth occurs by a combination of chemical vapor deposition and the scavenging of small clusters.

In further studies, emphasis was placed both on refining the model and on growing particles formed by homogeneous nucleation to $> 10 \mu\text{m}$ diameter to enable particle collection from the gas. The experimental apparatus design was based upon the following:

- (1) Particle generation by homogeneous nucleation.
- (2) Maintenance of conditions for CVD growth on the particles while significant supersaturation of the nuclei is prevented by dilution with additional silane. The rate of the gas phase reactions is limited to allow condensible products to diffuse to the particles' surfaces as fast as they are produced. A kinetic model was developed to describe the nucleation and growth process more accurately than previously had been possible.

A three-stage reactor was constructed to better control the reacting system and to provide additional data for correlations with the model. Seed particles, formed in the first stage, were grown to about $2 \mu\text{m}$ in the second stage and then to $> 10 \mu\text{m}$ in the third stage. The experimental separation between particle growth and runaway nucleation was found to be very sharp. A 17% increase in SiH_4 concentration, for example, was shown to cause a 10^4 increase in the number concentration of particles. Thus, small variations in operating conditions can result in catastrophic results. Under carefully controlled conditions, however, $> 10 \mu\text{m}$ particles were grown avoiding runaway nucleation. The particles could be fused in a high temperature zone for about 1 s, yielding densified particles more amenable to separation from the gas by aerodynamic means.

The model and the process for particle formation and growth are not restricted to the growth of silicon particles from silane. Other reaction systems can be used in this aerosol reactor and the process for particle production is applicable if the gas-phase, nucleation-reaction rate can be controlled and limited. Thus, powders of desired size particles of other materials can be grown in a similar fashion.

D. CHEMICAL ENGINEERING AND ECONOMIC ANALYSES

Contracts for independent chemical engineering analyses and economic estimates of the Task process-development program were instituted at Lamar University (JPL Contract 954343 and Texas Research and Engineering Institute (JPL Contract 956045). These

studies were to provide necessary additional information for evaluations and comparisons of the development efforts. Part of the chemical engineering analyses involved studies of the chemical, physical, and transport properties of the reactants and of the characteristics of the process systems. Extensive experimental and literature descriptive data were obtained for SiH_4 , SiCl_4 , SiHCl_3 , SiH_2Cl_2 , SiF_4 , and silicon, including the properties of critical temperature, critical pressure, critical volume, vapor pressure, heat of vaporization, thermal conductivity, heat of formation, Gibbs free-energy of formation, and gas viscosity for chemical reactants and intermediaries. The data were presented as functions of temperature to facilitate their use in research, process development, and production engineering analyses.

The chemical engineering analyses included activities for the formulation of the baseline conditions for the process being examined, including reaction chemistry, process flowsheet, material balance, energy balance, property data, equipment design, major equipment list, and production labor requirements. Detailed data for raw materials, utilities, major process equipment, and labor were given in the process design packages. These, in turn, formed the bases for the economic analyses. Primary results of the economic analyses were calculations of the plant capital investment and product cost, where the product cost includes the direct manufacturing cost, the indirect manufacturing cost, plant overhead, and general expenses. Market prices were calculated taking into account a profit measured in terms of the discounted cash flow or of return on investment.

Economic analyses involving preliminary process designs for 1000-MT/year production plants were completed for the following processes:

- (1) The Battelle Columbus Laboratories process for the Zn reduction of SiCl_4 in a FBR.
- (2) The conventional Siemens technology silicon chemical vapor deposition from SiHCl_3 .
- (3) The UCC process for generation of silane and its conversion to silicon.
- (4) The HSC process for the generation of SiH_2Cl_2 and the deposition of silicon in a modified Siemens reactor.

Cost and profitability estimates from these analyses are shown in Table 4.

E. HYDROCHLORINATION OF METALLURGICAL-GRADE SILICON

The importance of the hydrochlorination reactor in both the UCC silane process and the HSC dichlorosilane CVD process necessitated additional investigations to fully characterize the reactor and its operating

Table 4. Economic Analyses for Various Preliminary Process Designs for 1000-MT/Year Silicon Production Plants

Process	Product Cost \$/kg (1980 Dollars)	Sales Price \$/kg (1980 Dollars) 20% ROI ^a
Union Carbide	9.66	15.10
Battelle Case A ^b	12.08	19.50
Battelle Case B ^b	11.07	17.20
Conventional Siemens	53.77	-
Hemlock Semiconductor	22.65	37.80

^aReturn on investment.

^bCases A and B differ in the size and number of electrolysis cells.

conditions. These studies of the reactions of mgSi , H_2 , and SiCl_4 to generate SiHCl_3 consisted of:

- (1) Reaction kinetics as functions of temperature, pressure, and H_2/SiCl_4 feed ratio.
- (2) The effects of the Cu catalyst and the mgSi particle size on the reaction rate.
- (3) The dependence of the reaction characteristics on extended reaction times.
- (4) The behavior of candidate materials of construction in the corrosive atmosphere of the reactor.

The results and conclusions of these studies, carried out by MIT under JPL Contract 955382, were:

- (1) Conversion of starting material to useful product is essentially 100%. With rising temperature, the reaction rate increases rapidly and a higher conversion occurs. Although the rate of approaching equilibrium decreases with pressure, the conversion percentage increases. A higher SiHCl_3 yield takes place with increasing $\text{H}_2/\text{SiHCl}_3$ ratios, but the reaction rate is reduced.
- (2) Reaction rate is independent of silicon particle size in the range of >37 to $595 \mu\text{m}$. A 2 wt % Cu catalyst increases the rate twofold compared to the noncatalyzed reaction.
- (3) No change in reaction rate was observed after several hundred hours of reaction.

- (4) Type 304 stainless steel and Incolloy 800H showed no significant corrosion under the reaction conditions. Apparently, formation of a silicide film serves to protect the reactor wall. Thus, previously observed corrosion problems appear because of subsequent reactions in a moist atmosphere and not to the effects of the hydrochlorination reactions under controlled, dry conditions.

These studies provided substantial evidence that the hydrochlorination reaction can produce a high SiHCl_3 yield from mgSi . This reactor, therefore, offers an essential link for a closed-loop process in which mgSi is the basic feed material and H_2 and SiCl_4 are recycled byproducts of the process.

F. RADIANTLY HEATED FLUIDIZED-BED REACTOR

The objective of this research, by Professor O. Levenspiel at Oregon State University under JPL Contract 956133, was to examine radiant heating of the particles of a fluidized bed as the first step in consideration of alternative heating methods for the silane FBR system. Proposed advantages include avoidance of heating through the reactor walls to prevent deposition of silicon on the walls, the capability of conveniently separating the distributor from bed heating, and the likelihood of more efficient heating.

Two important characteristics of the system were evaluated. The first involved effective absorptivity of the bed, i.e., the fraction of electrical energy supplied to the heater that is absorbed by the bed particles. It involves the geometry and position of the heaters, the absorptivity of the bed, and the heat flow in the bed. Heat flow in fluidized beds is rapid and primarily dependent on the circulation rate of the bed solids and the bed configuration.

The second important characteristic evaluated was the heat transfer coefficient between the hot bed and the cool distributor plate. Reactor design depends on this factor.

All experiments were performed in a nonreacting system without silane. Conclusions from the experiments were:

- (1) The effective absorptivity of radiant energy by the bed and the heat transfer coefficient between the bed and the distributor are independent of the lamp power.
- (2) The bed absorptivity is:
 - (a) Only affected by bed height insofar as it changes the distance from the source.
 - (b) Increased sharply with gas velocity.
 - (c) Dependent on the reactor geometry. Designs yield higher values if they favor violent bed-bubbling with more particles ejected into the freeboard.

- (3) The heat transfer coefficient is dependent on the reactor geometry. The sequence of values is round > round-tapered > square-tapered > square.

These conclusions were applied to calculations for a scaled-up reactor operated under conditions of a 700°C bed and $<300^\circ\text{C}$ temperature at the distributor. The distributor temperature could not be maintained using either a square or a round configuration. Configuration options were a conical bed without a distributor, a multiorifice or multicone bed, and a tapered bed with the cross-sectional areas of the distributor and surface dependent on the energy level needed for the bed temperature. The rough estimate of energy use for the silane system using a multiorifice configuration was 0.4 kWh/kg silicon.

Demonstration of the feasibility of heating a FBR in this manner requires an extension of this study so that other factors could be investigated. Factors of concern include the proper particle size distribution of the bed, steady-state operating conditions, methods for the introduction of the seed and the removal of the product, materials of construction, and the proper radiation source for a specific system.

No further research in radiant heating of FBRs was carried out.

G. HYDROCHLORINATION OF METALLURGICAL-GRADE SILICON

This program, investigated by Solarelectronics, Inc., under JPL Contract 956061, was a continuation of the investigations performed under the JPL contract with MIT. It called for extended studies of thermodynamic properties and of reaction kinetics of the hydrochlorination reaction with larger ranges of pressure and temperature as the main variables. Study of corrosion phenomena under the reaction conditions for hydrochlorination was continued.

Studies of reaction kinetics showed that although the conversion yield of SiHCl_3 increases with pressure, the conversion rates decrease. The rate and yield increase both with temperature under isobaric conditions and with the H_2/SiCl_4 ratio. The overall reaction followed a pseudo-first-order kinetics model. Variation of the first-order rate constant with temperature gave a value of 13.2 kcal/mol for the activation energy.

Deuterium isotope kinetics effects revealed no isotope effects, indicating that H_2 is not directly involved in the rate-determining step of the reaction. Based on this result, a model of the reaction mechanism was proposed.

Corrosion tests were carried out for 87 h under reactor conditions of 300°C , 300 lb/in.² gauge, and a H_2/SiCl_4 feed ratio of 2.0. The system contained 0.5% HCl and a mixture of chlorosilanes. Materials

tested were carbon steel, Ni, Cu, Monel, 304 stainless steel, Incolloy 800H, and Hastelloy B-2. All of the samples gained weight because of silicide film formation. Analysis by SEM revealed diffusion of silicon into the base metal. The results showed that film depositions were greater for metals than for their alloys and that alloys with the higher melting elements permitted the least amounts of film formation. Thus, stainless steel, Incolloy 800H, and Hastelloy B-2 are suitable materials of construction for the hydrochlorination reactor.

Because studies of reaction kinetics demonstrated that the highest practical pressure and temperature are the best conditions for hydrochlorination of mgSi, UCC selected values of 500°C and 515 lb/in.² absolute. The corrosion data are expected to be useful in reactor design and in defining operating conditions.

H. MODELING OF FLUIDIZED-BED REACTOR FOR PRODUCTION OF SILICON FROM SILANE

This study, conducted at Washington University at St. Louis under JPL Contract 957158, involved the development of a mathematical model to simulate the silane FBR. The model also was to be usable for the systematic optimization of the reactor by:

- (1) Investigation of the sensitivity of the model to assumed constitutive relationships and parameter values.
- (2) Interpretation of the experimental data.
- (3) Prediction of the operating conditions and performance of the reactor.
- (4) Analysis of the reactor design.

The work tasks were:

- (1) To develop the phenomenological relations and constitutive equations to describe the reaction system.
- (2) To develop the model equations for the gas and solid phases.
- (3) To develop a computational algorithm for solving the model equations.
- (4) To compare predictions obtained from the use of the computer program with the experimental data.
- (5) To identify the primary parameters and outline a program to verify the model.

As the first step, the reaction paths for silane pyrolysis and silicon formation were reviewed, and the growth of seed particles by CVD and by the scavenging of fines was described. The homogeneous gas-phase sequence of reactions leading to the nucleation of fine particles and the growth of these particles by CVD and condensation of the nuclei was detailed. It was shown that CVD, and not diffusion, would be the rate-limiting step for particle growth in FBR.

Because the promotion of CVD on seed particles and the suppression of homogeneous nucleation to form fines was the desired operation-mode of the silane-FBR, the modeling effort used these paths as circumstances for analyzing the model. The modeling approach was on two levels. First, a model was developed based on ideal mixing of gas and solids, the continuous stirred-tank reactor (CSTR). Because perfect mixing and gas-solids contact are assumed, the use of this model gives an underestimation of the amount of fines produced and provides an upper limit for the rates of deposition on the seed particles.

The second model was derived from state-of-the-art models of bubbling reactors (FBBR), and a much more complete characterization was introduced. Grid, bubble, and emulsion regions were separately accounted for. The ratio of the jet-emulsion and bubble-emulsion exchange coefficients, which can be calculated from available correlations, was used as the one adjustable parameter. There is no adjustable parameter in the CSTR. Material and energy balances were written for each region, and exchanges between the regions were allowed.

Reasonable agreement was found between the predictions of the CSTR model and JPL experimental data, indicating excellent gas-solid contact in the reactor. However, the FBBR predictions only approached the experimental results at very high jet-emulsion exchange coefficients. Because the JPL experiments were short runs, however, the relatively small changes of the seed particle diameters limited the accuracy of the data. This prevented a sharp discrimination between the CSTR and FBBR models as well as an evaluation of the adjustable parameter of the FBBR model.

Parametric sensitivity analyses of model predictions indicated the reactor performance can be affected by feed rate, feed silane concentration, bed temperature, particle size, and reactor design. When adjustable operating conditions were fixed, reactor performance was dramatically affected by the distributor plate design and by the extent of gas-solid contact in the plate region. Good contact results in significant reductions of fines formation and elutriation. The choice of kinetic parameters for the various silane reaction paths had a less dramatic effect on reactor performance.

Interpretation of experimental results and quantification of the effects of design and operation variables on seed particle growth rate and fines elutriation were derivable from the FBBR model and the CSTR model provided an upper limit to the deposition rate on the seed particles. These types of analyses can be useful in planning experiments and obtaining data that can form the basis for optimizing reactor design and operating conditions. Complete verification of a model, however, will require:

- (1) Data for more substantial seed particle growth.
- (2) An improved model of the distributor plate region.
- (3) More reliable kinetic data for the different reaction paths of silane pyrolysis.

SECTION VI

Effects of Impurities on Silicon Properties and Solar-Cell Performance

A. EFFECTS OF IMPURITIES AND PROCESSING ON SILICON SOLAR CELLS

This program, conducted by Westinghouse R&D Center, under JPL Contract 954331, was for the study of the effects of impurities, processing procedures, and contaminant interactions on the properties of silicon and the performance of terrestrial solar cells. In turn, this relationship permits chemical engineering and production plant design analyses of requirements for process purification units.

During the program, Cz, float-zone (FZ), and polycrystalline ingots, prepared by Dow Corning Corp., as well as dendritic web ribbons, were grown with controlled additions of impurities, using boron and phosphorus as the electrical dopants. Impurity elements included those present in mgSi, the raw material used for many refining processes, and those impurities that might be added adventitiously from subsequent processing in the production of single-crystal ingots, wafers, and solar cells. The elements studied as impurities were Au, Ag, Al, C, Ca, Cr, Co, Cu, Fe, Mg, Mn, Nb, Ni, Pd, Sn, Ta, Ti, V, W, Zn, and Zr. Impurity concentrations ranged from 10^{11} to 10^{18} atoms/cm³.

A functional analytical model was formulated in Phase I of the study. It was consistent with the hypothesis that impurity atoms act independently and primarily degrade minority-carrier recombination lifetime and reduce the short-circuit current of a solar cell. The cell parameters of open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), and cell efficiency were related to the concentrations of the impurities. Data, obtained from 52 Cz ingots and 44 dendritic web specimens deliberately doped with particular impurities, were shown to conform closely to the model. Effects of different impurities were distinctive and varied greatly. For example, a 10% decrease in baseline cell efficiency was caused by as few as 10^{12} atoms/cm³ of Ti or V while more than 10^{15} atoms/cm³ of Cu were needed for the same effect. The behavior of multiply doped materials and cells was successfully predicted using the model and experimentally measured relations of lifetime and efficiency values.

By using crystal-growth impurity-partitioning behavior and the relationships derived in this study for the effects of specific impurity concentrations on solar cell properties, tolerable impurity concentrations for a polycrystalline material feedstock for Cz processing were estimated. As a consequence of the specific effects on cell performance (Table 5), the degree of impurity toleration in the feedstock is primarily species-dependent. The limiting condition for acceptable purity for a certain crystal growth rate depends on the selected solar-cell performance level and not crystal breakdown.

Rather than sequential feeding, continuous feeding is advantageous when using a melt-replenishment method because of differences in the impurity build-up as a function of the volume of crystal grown. The yield of single-crystal ingot, however, is dependent on the total impurity concentration and on the conditions of ingot diameter, rate of pull, and melt-replenishment strategy.

Table 5. Calculated and Measured Relative Cell Efficiencies for Ingots Used to Model "Solar Grade" Feedstock

Impurity	C_O		C_S	
	10^{19}cm^{-3}	ppma	10^{14}cm^{-3}	ppma
Cr	0.73	146	0.8	0.0016
Mn	0.62	124	0.8	0.0016
Ni	1.60	320	5.0	0.01
Ti	0.017	3.4	0.0033	—
V	0.015	3.0	0.06	—
Total	2.97	596	6.6	0.0132
$\eta/\eta_O(\text{calc}) = 0.93 \pm 0.02$ $\eta/\eta_O(\text{meas}) = 0.89 \pm 0.03$				
Al	0.0033	0.66	10	0.02
Cr	0.18	36	0.2	0.0004
Cu	0.10	20	8	0.016
Fe	0.31	62	0.2	0.0004
Mn	0.15	30	0.2	0.0004
Mo	0.33	66	0.0015	—
Ni	2.50	500	8	0.016
P	0.0003	0.06	9	0.018
Ti	0.02	4	0.004	—
V	0.01	2	0.004	—
Zr	0.46	92	0.004	—
Total	4.0	804	35.6	0.071
$\eta/\eta_O(\text{calc}) = 0.89 \pm 0.03$ $\eta/\eta_O(\text{meas}) = 0.83 \pm 0.03$				

The efficiency of a typical baseline device is η_O , about 10% without AR coating.)

Phase II studied the effects of thermal treatments, crystal growth rate, base doping concentration and type, grain-boundary structure, and carbon-oxygen metal interactions. Data from more than 4000 cells firmly established that impurity-induced cell-performance loss is primarily caused by the reduction in base diffusion length. An analytical model based on this conclusion was developed to predict cell performance as a function of metal-impurity content for both n-base and p-base materials.

Only the data for Fe, Cu, and Ni deviated from the model. Detailed current-voltage studies coupled with metallography indicated that these variances were caused by junction excess currents induced by precipitates. Figures 10 and 11 show the relationships of specific impurity concentrations to solar-cell performance decreases. For the impurities Ti, V, Cr, and Mn, considerably less cell-performance reduction occurred in n-base cells. The data to demonstrate that this is a general conclusion were not obtained. Experiments indicated that efficiency reductions are nearly the same for the same impurity concentrations in low- (0.2 ohm-cm) and high- (4 ohm-cm) resistivity p-base cells. This led to the hypothesis that in the low-resistivity material, band-gap narrowing combined with the creation of excess numbers of traps (compared to the high resistivity material) compromise the beneficial effects of the larger V_{OC} .

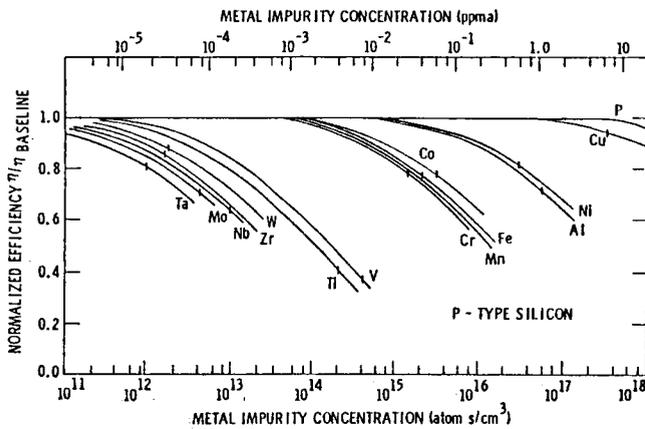


Figure 10. Impurity Effects on Cell Performance

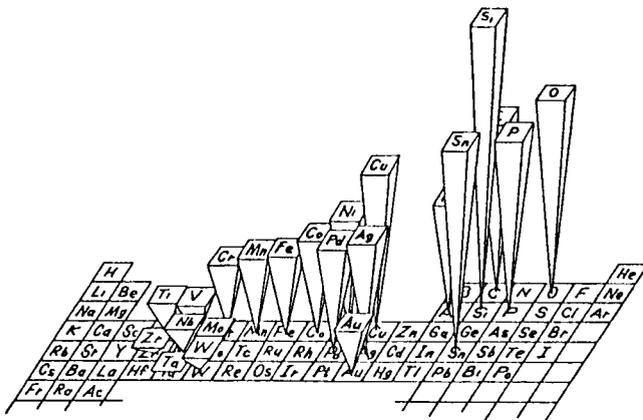


Figure 11. Impurity Effects on Cell Performance: Pictorial Representation of Comparative Values

In preliminary studies with polycrystalline cells, decreases in cell performance were shown to be impurity-species-sensitive. Large fractions of the impurities were found to be segregated at the grain boundaries.

Trade-off analyses, using data for cell efficiency-impurity effects, were proposed to determine polysilicon impurity concentration limits for processing steps. For single-crystal growth methods that involve large segregation coefficients, e.g., Cz and dendritic web, the limits were estimated to be about 1 ppba for elements such as Ti, which cause severe efficiency degradation, and as much as 100 ppma for relatively innocuous elements such as Ni. A scheme was developed to enable determinations of acceptable impurity limits as functions of the assigned cell efficiency, crystal growth method, melt replenishment strategy, and cell process sequence.

In Phase III, studies were continued of the effects of thermochemical gettering treatments, base dopant concentration and type, and grain boundary-impurity interactions, along with investigations of the effects of non-uniformity of impurity distribution, long-term presence of impurities, and synergistic-complexing phenomena. Gettering action was shown to be directly dependent on the magnitudes of the diffusion coefficients of the impurities. No evidence was found to indicate large effects of nonuniform impurity distribution on cell performance for variations of $\pm 10\%$. Data obtained for aging experiments at high temperatures showed that additional decreases in cell performance are functions of diffusion rates. Projected stabilities for Mo and Ti are greater than 20 years.

Detailed analyses of some polycrystalline cells showed that the relationship of the impurity concentration and lifetime within grains was similar to that obtained for single-crystal material. Electrical activity of impurities decreased because of precipitation in the vicinity of grain boundaries, and this reduction was directly related to the specific impurity diffusion coefficient.

The extensive database and the model equations derived in these studies can be used for the assessment of the usefulness of a silicon material, with a specific composition, for a specific process sequence and desired end use. Conversely, these results also allow the specification of material composition ranges and process sequence variations for desired end uses. Preliminary analyses derived from an extension of the impurity-effects model to high-efficiency PV cells indicated that the sensitivity of cell performance to impurities would increase. The increased sensitivity would be found in wide-base cells and medium-base cells with back-surface fields or passivated surfaces, but would be significantly reduced in cells with narrow (about 100 μm) base widths.

These studies have provided experimental data and analytical models to explain the effects of impurities on the properties of silicon materials and the performance of PV cells. This was done for many cases of interest to the research and industrial communities. In some cases, the descriptions are limited and the conclusions are not yet proven to be universal. In

these latter instances, the scope of the studies needs to be extended. Specifically, the area of high-efficiency cells needs to be investigated fully to characterize impurity effects for advanced-stage cells.

B. EFFECTS OF IMPURITIES ON SILICON SOLAR CELL PERFORMANCE

This program, carried out by Monsanto Research Corp. under JPL Contract 954338, was to study the correlation of impurity concentrations with the performance of solar cells. Single-crystal ingots doped with controlled amounts of Al, C, Cr, Cu, Fe, Mg, Mn, Na, Ni, O, Ti, V, or Zr, were prepared using the Cz and FZ procedures. Energy-conversion efficiencies were measured against a standard solar cell. Most impurities caused some degradation of cell efficiency. The most severe occurred in the presence of Ti, V, or Zr. Using a 10% decrease in efficiency as a criterion, the permissible impurity concentrations were shown to vary greatly for p-on-n cells made from FZ silicon material. For example, the values (in 10^{15} atoms/cm³) were: 0.02 for Ti, 0.2 for V, 2.0 for Zr, 5.0 for Cr, 6.0 for Fe, 20 for Ni, 80 for C, and 50 for Al.

A model was developed to allow comparisons of impurity concentrations and values of the minority carrier recombination lifetime. A direct relationship between cell efficiency and lifetime was shown. Comparisons of the cells made from Cz and FZ materials indicated that the efficiencies of the baseline p-type cells (made from undoped silicon) were about 12% more efficient for the baseline Cz cells and that FZ cells with secondary impurities were about 18% more efficient than the equivalent Cz cells. This difference in performance was related to the differences in oxygen and carbon content. There was a close correlation between base material minority carrier lifetime and cell efficiency. Diffusion and other processing steps caused parallel changes in these values for materials containing impurities. This result indicates that the measured quantities for solar cells, whether fabricated from pure or contaminated materials, are sensitive to the cell-processing conditions. For example, the minority carrier lifetime was found to increase during the diffusion step for materials containing Fe, Cr, and Mn. The presence of oxygen at a concentration of about 10^{18} atoms/cm³ in Cz silicon and $<10^{16}$ atoms/cm³ in FZ silicon seemed to affect the fill factor, which was found to be an average of 8% higher in the low-oxygen cells. Extended studies were recommended to determine the effects of processing on silicon materials, oxygen on impurities in silicon, impurities on n-base materials, and the presence of more than one impurity.

C. LIFETIME AND DIFFUSION-LENGTH MEASUREMENTS

Obtaining accurate, sensitive, and reproducible data for minority carrier recombination lifetime and diffusion length was essential in the investigations of impurity effects on cell performance by Westinghouse,

et al. A study, conducted by Northrop Research and Technology Center under JPL Contract 954614, was to assess the applicability of specific measurement methods to various ranges of values, to determine the characteristics of these measurements, and to associate the interconsistencies of the methods.

The first task was to verify the mutual consistency of the different measurement techniques. Minority carrier lifetime was measured using the method of transient photoconductivity decay (PCD) and steady-state photo-conductivity (SSPC). Diffusion lengths were determined on solar cells and other test structures by short-circuit measurements using either point-source excitation from a ⁶⁰Co gamma source or band-edge light.

There was excellent agreement between a bulk measurement and a device measurement of diffusion length, and moderate agreement between the diffusion-length equivalent lifetime and the lifetime measured by photoconductivity decay. In the course of establishing the generation rate in the SSPC method, earlier conclusions were confirmed concerning errors induced into bulk lifetime measurements by trapping effects, despite the use of background light to fill the traps. The disagreements between the measurements of the diffusion length lifetime and the PCD lifetime in the p-type sample was found to be consistent with trapping effects on the lifetime measurements. Some fast trapping was present in all of the bulk samples measured, and this conclusion was demonstrated by the fact that considerable background light was required in all cases to fill traps in SSPC measurements.

The bulk lifetime data, obtained by steady-state photoconductivity measurements for the impurity-doped samples (from the JPL contracts with Westinghouse, Dow Corning, and Monsanto), confirmed the extreme sensitivity of lifetime to the presence of Ti, Cr, Fe, and Zr. The cases of Fe and Cr were especially well-behaved in that the concentration dependence approximated the (-1) slope. For V, Mn, and Mg, the apparent lifetimes were larger for the more heavily doped specimens, thus indicating trapping effects on the measurements. The lifetimes seemed to be considerably less sensitive to the presence of Al, Ni, and Cu. In the case of Ni, and possibly Al, this may have occurred because of the low fraction of the total concentration that is electrically active.

The lifetime data derived from diffusion length measurements on devices indicated that lifetime is most sensitive to the presence of Ti, V, Fe, Cr, and Mn. A much smaller sensitivity was found for Al and Cu. Insufficient data were available to characterize Zr and Mg. Data for devices indicated somewhat greater sensitivity to the presence of Cr, Ti, and Ni than was observed in the bulk samples, although sensitivity to Fe in the device data was considerably reduced. General agreement was found with the conclusions of the Westinghouse and Monsanto studies regarding the sensitivities of these values to the presence of various impurities.

The results of this measurements program were:

- (1) Verification of the consistency of values among the very different experimental methods for measuring lifetime and diffusion length.
- (2) Establishment of the SSPC method for measurements to about 10 ns as well as under conditions of interference from minority carrier trapping and surface recombination.
- (3) Verification of the extreme sensitivities of lifetime values to the presence of specific impurities and the concentration dependencies found by others.

D. STUDIES OF THE EFFECTS OF IMPURITIES

This program of theoretical and experimental studies, investigated by C.T. Sah, Inc. under JPL Contract 954685, was directed toward determining the effects of impurities on the properties of silicon and on the characteristics of solar cell performance. The studies took into account impurity effects on impurity-related energy levels and on the density of the energy levels and recombination-generation properties of electrons and holes at the energy levels. The objectives of the studies were to develop a mathematical model for the prediction of impurity effects on cell performance and to conduct theoretical and numerical analyses of the effects of specific impurities and processing steps.

In the first phase, mathematical and computer models were developed for the one-dimensional solar cell diode. A transmission-line-equivalent circuit model was formulated for computation of the exact steady-state characteristics. Effects that were studied are the substrate dopant impurity concentration, second-coupled recombination level, spatial variation of the recombination-center density and diffused surface impurity concentrations on the maximum intrinsic efficiency, short-circuit current, and V_{OC} . A new technique was suggested for the measurement of the base lifetime using a small-signal transient under illumination at the short-circuit maximum-power condition to provide better lifetime-cell performance correlations.

Using the model, solutions then were obtained in studies of the effects on cell performance of interband Auger recombination, surface recombination at the contact interfaces, enhanced impurity solubility, diffusion profiles, and defect impurity-recombination centers. Specific cases were considered of Ti and Zn as impurities in high-efficiency back-surface field (BSF) cells.

Also investigated were the complex dependences of the peak conversion efficiency of a BSF solar cell on thickness and on the concentrations of recombination and dopant impurities. More than 100 computer-aided

cell designs were obtained using the transmission line-circuit model to solve the Shockley equations. A broad maximum, which varies less than 1% over more than a 3:1 range of cell thickness from 30 to 100 μ m, was found for the efficiency-thickness function. An optical reflecting back surface gave only a slight improvement in this thickness range.

The effects of electrical short circuits across the BSF junction at the perimeter of a cell were analyzed by applying low-level, one-dimensional analytical theory to a developed cell geometrical device model. For small-area, thin, large-base-diffusion-length cells, the reduction in V_{OC} and efficiency can be so large that the edge defects almost completely nullify the performance improvement obtained using the BSF junction.

Another analysis dealt with quantitative effects of cell thickness, defect area, defect density, and interface or surface recombination velocity at the defective area on the V_{OC} of a BSF solar cell. A developed perimeter device model was used to show:

- (1) Decrease in V_{OC} is nearly independent of the defect area with a dimension less than about 30% of the minority carrier diffusion length in the base.
- (2) Decrease in V_{OC} is mainly caused by the density of the defect.
- (3) The presence of only one defect of small area across the BSF junction will cause significant reduction in the V_{OC} of a high-efficiency cell.
- (4) Reduction in the V_{OC} , as a consequence of defects across the BSF junction, increases as the cell is made thinner.
- (5) A defect area acts essentially as an electrical short circuit across the BSF junction.

The conclusion of this study was that material and fabrication defects across the BSF junction of high-efficiency cells (even the presence of one defect) can be the major obstacle to high V_{OC} and high efficiency.

In the study of the exact numerical solution of the dependence of the fill factor and efficiency in impurity-doped BSF cells on cell thickness, two new features, not predicted by the low-level analytical theory, were shown to be associated with the high-injection-level effect in the base. A new theory was developed to distinguish an acceptor-like deep level from a donor-like deep level using measurements of thermal-emission and capture cross-sections. Using the measured emission-capture cross-section ratio, the theory also describes the magnitude of the lattice distortion around an impurity atom before and after the capture or emission of an electron or hole at the impurity center. These studies are continuing.

E. CELL MEASUREMENTS OF IMPURITY EFFECTS

The purpose of this program, investigated by Solarex Corp. under JPL Contract 955307, was to obtain data concerning effects of impurities on performance of solar cells fabricated and measured by a commercial cell manufacturer. To ensure the validity of the overall conclusions of the Task program on the effects of impurities, these separately determined data and conclusions were compared with the information secured by Westinghouse and Monsanto. The cells were fabricated and analyzed using aerospace technology and quality-assurance procedures to ensure that measured variations of cell performance were caused by impurity effects. Wafers were prepared from deliberately doped Cz single-crystal ingots. Cells fabricated from uncontaminated semiconductor-grade silicon were used as verification cells to establish the baseline process, as monitor cells to establish a clean processing system, and as control cells to correlate performance measurements. These cells had average air mass zero (AM0) efficiencies of nearly 13% at 25°C. No cross-contamination of control or monitor cells was observed. Performance degradation in the test cells principally was caused by impurity contamination, and a definite dependence on concentration was observed for some impurities. Additive effects for more than one impurity were seen. Performance degradation, even at the very low concentrations of 0.033×10^{15} , 0.4×10^{15} , and 0.008×10^{15} atoms/cm³, was caused by Ti, V, and Ta. Cell performance seemed relatively insensitive to the presence of Cu, C, Ca, Cr, Fe, and Ni. These results generally verified the measurements performed by Westinghouse on the same materials.

F. CELL MEASUREMENTS OF IMPURITY EFFECTS

The purpose of this program, conducted by Spectrolab, Inc. under JPL Contract 954694, was to obtain data on the effects of impurities on performance of solar cells fabricated and measured by a commercial cell manufacturer. To ensure the validity of the overall conclusions of the Task program on the effects of impurities, these separately determined data and conclusions were compared with the information secured by Westinghouse and Monsanto. Using conventional aerospace process technology for solar-cell fabrication, 63 lots of wafers from single-crystal ingots deliberately doped with impurities were studied. The silicon sources were Dow Corning-Westinghouse crucible-grown silicon, Monsanto crucible-grown silicon, and Monsanto FZ silicon. In the measurement procedure, quality control was monitored, and cross-contamination was prevented. Cell performance was determined by electrical and

spectral measurements. Except for one case, the properties of cells within each impurity concentration group were extremely consistent electrically and spectrally. There was good correlation between electrical outputs and spectral response data. Elements that caused decreases in efficiency were Al, Cr, Fe, Ni, Ti, V, and Zr. For the last three of these elements, concentration levels below 10^{13} atoms/cm³ appreciably affected efficiency. In many cases, because more exact concentration data were not available, performance losses could only be related to impurity limits. Less than 10% efficiency degradation occurred at the concentrations used for Mn, Mg, C, and Na. There were tentative indications that the presence of Cu ameliorates the effects of other impurities. The result generally verified the measurements performed by Westinghouse on the same materials.

G. COMPOSITION MEASUREMENTS BY ANALYTICAL PHOTON CATALYSIS

The object of this research, carried out by Aerospace Corp. under JPL Contract 955201, was to assess the applicability of the photon catalysis technique for composition analyses of silicon samples. The technique was evaluated both as a detector and as a concentration measurement technique for Al, Cr, Fe, Mn, Ti, V, Mo, and Zr impurities. The best fluorescence lines to monitor were established, and initial sensitivities for each of these elements were determined by atomic absorption calibrations. In the course of these tests, vapor-pressure curves for six pure substances were mapped. The detection of these impurities in silicon matrices was studied. The evaporation process was shown to be congruent. Thus, the spectral analysis of the vapor yields the composition of the bulk sample. In addition to the data acquired in doing these mainline tasks, much ancillary information was obtained. Emission signatures were determined for several additional elements: As, Bi, B, Ca, Cu, Ga, Ge, Mg, Na, P, and Pb. Ionic emission lines for Ca and Mg were determined to be useful for analysis. Pulsed sample introduction was examined, and it was found that as little as 1 nanogram of Pb is detectable in a single shot. The conclusion reached from these studies was that the photon catalysis technique is suitable for the bulk analysis of solar-grade silicon. The ancillary data also suggest that gaseous feedstocks in the form of metal hydrides can be analyzed by this technique and that pulsed sampling techniques are compatible. This last conclusion suggests the possibility of developing a surface-analysis instrument by combining laser microprobe and photon catalysis technologies.

SECTION VII
JPL In-House Research

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The research program conducted in the JPL laboratories was patterned after the Silicon Material Task program. Thus, one primary section investigated reactions and reactor technology for low-cost polysilicon processes, and the other characterized the effects of impurities on the properties of silicon materials. Chemical engineering studies were directed toward research involving a silicon deposition reactor for the silane process. Thus, this research was complementary to the effort on the development of this reactor under the JPL contract with UCC. Research on impurity effects was done in collaboration with similar studies being conducted under JPL contracts, especially those with Westinghouse, Monsanto, and C.T. Sah Associates.

A. SILANE DEPOSITION REACTOR INVESTIGATIONS

The JPL chemical engineering effort was limited to studies of chemical reactors suitable for the conversion of silane to silicon. This was a consequence of early conclusions of the Silicon Material Task that the silane process had a high probability of achieving the Task goal and that the development of a deposition reactor for the silane process would be a formidable problem. Three types of reactors were studied: the FBR, the FSR, and the silane-to-molten silicon reactor (SMSR). The most intensive effort involved the development of the FBR.

The FSR was the reactor of first choice by UCC, and its development was emphasized in the early period of the UCC contract. At JPL, research on this type of reactor was carried out using the CFP (Figure 12). In this reactor, auxiliary flows of H_2 through the upper reactor wall and through the heater element were intended to prevent silicon deposition on the walls. In conjunction with experimental studies, a theoretical analysis was formulated to provide a quantitative description of the kinetics of the heterogeneous pyrolysis of silane at relatively low temperatures. The proposed mechanism involved a sequence of homogeneous gas-phase reactions, the coagulation of particle clusters, and the decomposition of silane on the clusters. The large surface area necessary for heterogeneous pyrolysis is provided under conditions in which rapid generation of very small particle clusters occurs. The kinetics of silane decomposition are rapid enough, even at low temperatures, to give practical production rates. Analytical treatment yielded a general equation for heterogeneous pyrolysis and a specific equation for the conditions of a FSR.

The influences of temperature (800 to 850°C) and silicon seed particles on the formation and growth of silicon particles from silane pyrolysis were determined in a brief experimental study. Conditions of gas flow,

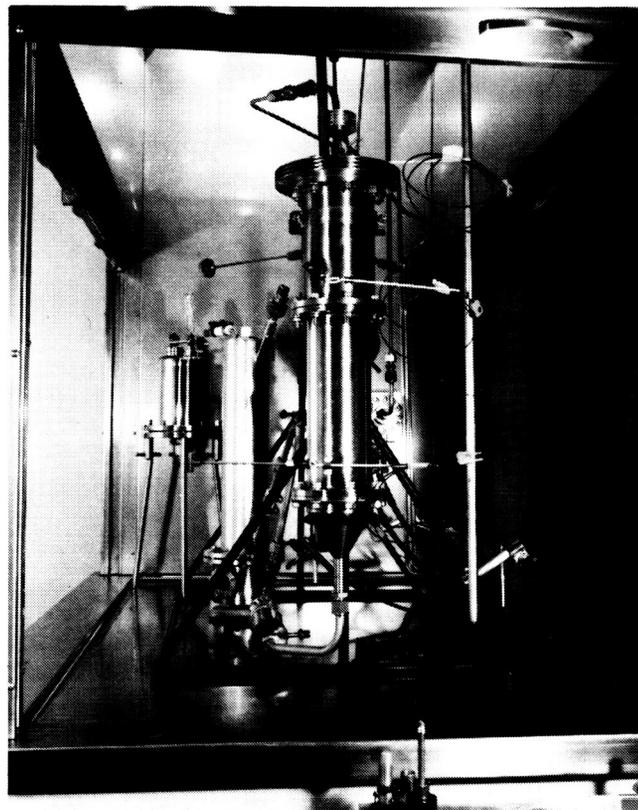


Figure 12. JPL CFP Reactor

pressure, and silane concentration (4%) were kept constant. Using SEM descriptions of the particles, it was concluded that no CVD took place on unheated seed particles introduced into the system. The main product was a fine powder (about 0.1 μm diameter) formed by homogeneous gas-phase nucleation. Some dense, thin deposits also formed on the hot reactor surfaces by CVD.

The experimental results were described mechanistically using a general concept in which successive gas-phase reaction steps occur. A correspondence was shown between the model and the experimental results, because the values of experimentally obtained reaction-velocity constants and surface-reaction efficiency seemed to support the mathematical model. Other models of the overall mechanism, however, may be as valid. This work was terminated in favor of emphasis on the development of the FBR for the silane process.

The laboratories of UCC and JPL carried out collaborative efforts to develop FBR technology for the silane-pyrolysis system. The effort at UCC dealt mainly

with the objective of defining reactor design and conditions for steady-state, long-term operation at silane concentrations of about 20% in H₂ that were commensurate with suitable silicon yield in a satisfactory form, high-mass throughput, and acceptable product purity. The effort at JPL, however, was centered on obtaining a description of the silane-to-silicon deposition process in a FBR under conditions of very high silane concentrations, including 100%. The JPL research also focused on developing the means for the preparation of suitably pure seed material and for reducing the loss of silicon because of the formation and elutriation of fine particles. Considerable differences in reactor design and operating conditions resulted from the drives to achieve these separate, but complementary, objectives.

The FBR effort at JPL preceded the UCC research. The JPL team began planning an in-house program early in 1976, after it concluded that a low-cost silane-to-silicon process could not be secured using a Siemens CVD-type reactor as the pyrolysis-deposition reactor and recognizing that the development of a different reactor was a formidable technical task. Preliminary analyses of the characteristics of silane pyrolysis, of a model for a silane-FBR system, and of a development program plan were discussed in February 1976. The plan outlined a 1-year study and contained work tasks for a chemical reaction analysis, reactor modeling, cold-flow fluidization experiments, and chemical engineering studies with small diameter FBRs.

The first step of the FBR development program was to perform a series of theoretical studies to model the reactor in the silane reaction system. The purpose was to provide an outline for a research plan and the basis for the interpretation of the data to be obtained in the experiments.

The first phase of the modeling effort was described in June 1977. Although mass transport, particle growth, and fluidized-bed behavior were considered, the path of homogeneous gas-phase reactions was neglected in favor of sole dependence on a heterogeneous surface reaction. The inappropriate use of this and other assumptions was pointed out in a review of the model by a consultant, Professor T. Fitzgerald of Oregon State University. This model, however, served as a start for refinements based on analyses of experimental data.

Integrated mathematical models were developed to describe silicon particle growth. The assumption was that particle growth was the direct result of heterogeneous deposition. The depositing particles resulted from a sequence of gas-phase reactions forming silicon nuclei and then of the clustering of the nuclei into very small particles. A diffusional growth mechanism, used as the basis for the model, emphasized the need for rigorous experimental information regarding the mechanisms and kinetics of silicon parti-

cle growth. The conclusions from these studies provided an impetus for the use of expanded sets of operating conditions for an experimental reactor. Later, coupled with experimental results, the models provided the basis for revised concepts of the growth mechanisms in the FBR system.

The first FBR experiments were done in a 1-in.-ID reactor, although the narrow reactor was ill-suited for the experiments because it precluded a well-fluidized bed. The objective was to determine whether reasonable concentrations of silane could be used without generation of large amounts of fine particles, an undesirable condition for FBR operation. The limiting silane concentration of 1% under epitaxial deposition conditions, which had been cited in a previous study, was surpassed in these experiments that used concentrations up to 15% silane in H₂. The temperature range was 550 to 700°C, and fine-particle formation was 2%. These preliminary results, albeit obtained in a reactor that was not performing in a well-bubbling fluidized mode, gave indications that a reactor could be run with >10% silane concentrations. A concentration of 10% was a milestone, because an economic analysis had indicated that at 10% silane an FBR would have the high throughput and low energy-use attributes necessary for reaching the Task economic goal using the silane process.

The next experimental study, using a 2-in.-ID reactor, was to establish a window for reactor operation to: (1) study the effects of temperature, concentration, flow rate, and pressure; (2) relate experimental conditions to the problems of dust formation, clogging, and bed slugging; and (3) to develop and test equipment and instrumentation. This was intended to provide the description of the operating conditions for a 6 in. FBR study that was to follow. A recurrent problem was the formation of clogs which prevented proper operation of the reactor and forced cessation of runs. The loosely bound type of clog appeared in regions of the bed that did not have good fluidization. The dense clogs seemed to be temperature dependent, occurring mainly in regions between 650 and 700°C, probably as a consequence of the sintering of fine particles. Inadequate fluidization also was believed to be involved. Two forms of surface deposition were found. At temperatures between 500 and 600°C, the deposits were fairly dense and granular. At high concentrations, flocs were observed on the surface. High temperatures produced a nodular, dense growth and, in some cases, fine fibers were found. Submicron fine particles of 0.2 to 0.8 mm diameter agglomerated into large masses were found to increase with concentration. These experimental results led to intensified efforts to determine conditions to eliminate clogging and to keep fine particle formation to a minimum.

Continued studies with the 2-in.-ID reactor revealed that clogging can be avoided by keeping the gas velocity greater than $U/U_{MF} = 8$ at 10% silane in H₂.¹ Complete silane pyrolysis occurred in the temperature

¹ Definition of U/U_{MF} = actual gas velocity/gas velocity for minimum fluidization.

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range of 680 to 720°C for concentrations up to 15%, and no excess elutriation of fines occurred with velocities as high as $U/U_{MF} = 12$. This was the first evidence that a scavenging mechanism for the removal of the fine particles by the large seed particles could be involved. The scavenging action is facilitated by the proper design of the distributor plate and the positioning of the temperature zones. Tiny gas bubbles formed by the grid enable efficient heat transfer and ready capture of the clusters by the seed particles. A sufficiently high temperature just above the grid allows the complete decomposition of the silane near the grid and a long residence time for capture. (The deliberate removal of fine particles by using a FBR had already been reported for other systems.) Based upon further observations from SEM and density measurements of dense depositions, a particle growth mechanism was proposed involving the combined actions of CVD and scavenging of fines. The study with the 2-in.-ID reactor provided information for the operating conditions for a larger silane-FBR. Also, short runs using silane concentrations ranging from 20 to 100%, gave encouraging results that high silane concentrations were usable without causing the formation of unacceptable amounts of fines. Some difficulties in fluidizing the 2-in.-ID reactor remained, however. A 6-in.-ID reactor was designed and fabricated based on the analysis that data obtained from a 6-in. reactor could more surely be used for evaluation, optimization, and scale-up design. The study using the 2-in.-ID FBR was summarized in December 1978.

A 6-in.-ID FBR was used in the third phase of this research (Figures 13 and 14). The first objectives were:

- (1) To design a cooled distributor plate to maintain operating conditions necessary to prevent silane decomposition in the distributor by controlling the plate temperature to $< 400^{\circ}\text{C}$ concurrently with a bed temperature of 650°C .
- (2) To determine the feed-concentration limit and the operating conditions for dense, coherent particle growth and minimum fine particle formation.
- (3) To obtain kinetic data to be used for formulation of a model for the deposition mechanism and the operation of the FBR. After a series of modifications to obtain effective cooling of the plate and adequate heating of the bed, the reactor was shown to operate satisfactorily without episodes of clogging or plug formation. In the final design, the stainless steel 6-in.-FBR was 48 in. high, had a 24 x 24 in. expanded head, and used one or two layers of 325 mesh stainless steel screen supported by a perforated plate as the distributor plate. The plate was water-cooled to maintain its temperature below 350°C to prevent silane decomposition in and clogging of the pores of the grid. The 650°C reaction zone starts at about 3 in. above the plate. To maintain a constant bed height, product removal was done by using a fluidized tube attached to the bottom of the reactor.

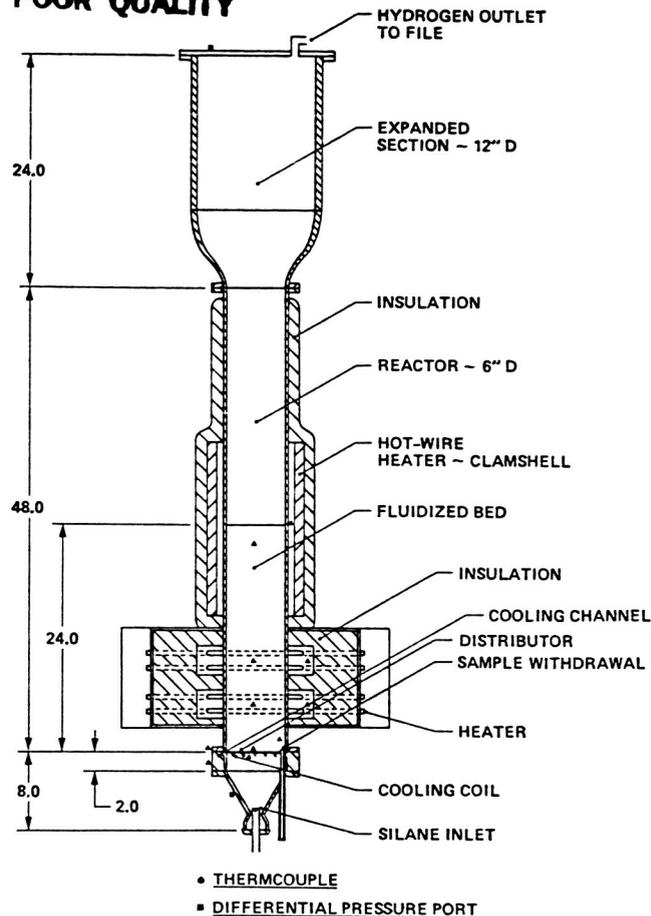


Figure 13. Fluidized-Bed Reactor (6 in. ID)

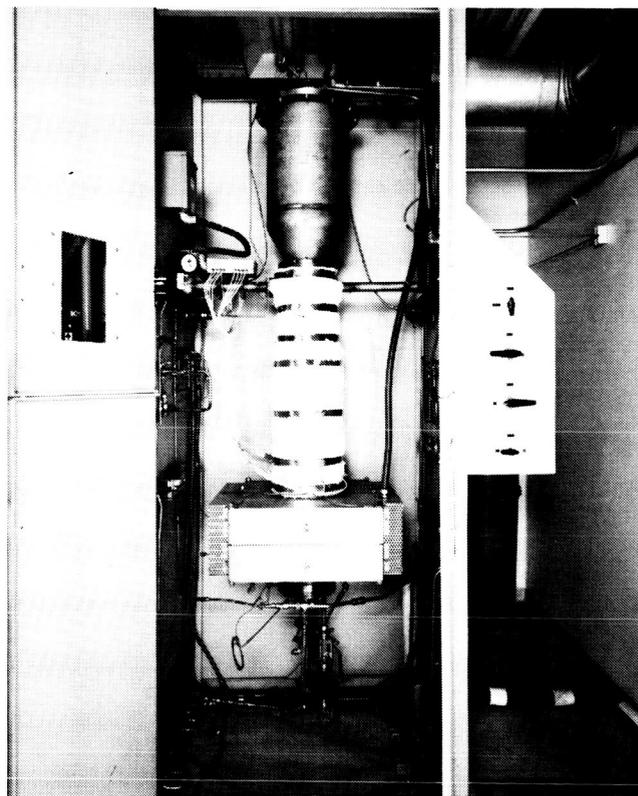


Figure 14. JPL Fluidized-Bed Reactor

A series of experimental runs, conducted for times ranging from 30 min to about 3 h, demonstrated the capability of efficiently converting silane to silicon deposited in the bed. These runs investigated the effects of parametric changes and reactor modifications and were thus necessarily limited in time. Suitability of the reactor design was demonstrated, because the experiments were at high silane concentrations and no plugging occurred nor were excess fines produced. The silane conversion efficiency was essentially 100% when the bed temperature was kept at 650°C. More than 90% of the product silicon was deposited in the bed, and the losses by elutriation of fines ranged between 6 and 10% for high silane concentrations (including 100%). The maximum silicon production rate was 3.5 kg/h for a 3-h-run using a SiH₄ feed concentration of 80% and a U/U_{MF} of 5.0. A product removal rate of 3 kg/h was demonstrated. Despite these successes, the dual objectives of demonstrating a technique for producing pure, suitably sized seed particles and of obtaining a high purity product were not achieved in this series of experiments. The final phase of the JPL effort centered on these two objectives.

The neutron activation analysis (NAA) data for the chemical composition of the bed particles taken from the UCC FBR and the JPL FBR showed heavy contamination, especially by the elements-of-construction of the reactors. The ratios of the concentrations of the main elements of the reactors (Fe, Cr, and Ni) were nearly replicated in the ratios of the concentration measurements of the bed particles.

Two ways were considered to prevent the introduction of wall material into the bed. Insertion of a barrier liner was chosen for immediate experimental trial rather than the alternative of fabrication and instrumentation of an entire reactor composed of a relatively impurity-free material, such as quartz.

A critical review of the problem and the proposed solution was held at JPL in March 1984. Dr. J. Routbort, an expert in abrasion technology from the Argonne National Laboratory, and Dr. T. Fitzgerald, an expert in fluidized-bed technology, were consultants who joined the FBR teams of UCC and JPL in the review. The likelihood of abrasive action by silicon particles and the probable rate of abrasion of the reactor walls were discussed in the context of the designs and operating conditions of the reactors. The erosion rates for liners fabricated from silicon and quartz were calculated by Dr. Routbort. Using the set of worst operating conditions described by the experimental teams, the rate was 1.3×10^{-7} cm/s for a silicon liner, equivalent to a 1700-h lifetime of operation assuming an 0.8 cm wall thickness. The lifetime for a quartz liner was calculated to be 640 h of operation. These estimates provided the basis for concluding that the use of liners would probably be economically practical. Experimental programs, therefore, were to concentrate on establishing high purity operation with liner-equipped reactors.

The quartz liner, mounted with a specially designed seal, was shown to maintain its integrity without collecting any silicon deposition after 4 h of operation using silane concentrations up to 50%. The silicon mass-balance data were very similar to those obtained previously without the liner. Although the composition measurements by spark source mass spectroscopy indicated that all metallic impurity concentrations were below the detection limits, the data did not yet establish a purity equivalent to semiconductor-grade polysilicon.

Concurrent with the experiments using a quartz liner, methods were developed using a jet milling device for producing suitably sized seed particles from polysilicon chunks and for cleaning the surfaces of these particles. These procedures were shown to be feasible, but a demonstration of applicability for large-scale production of clean seed particles remains to be done.

The JPL in-house program to develop FBR technology for the silane process ended in June 1985. A final report on the last phase of this work was issued in April 1986.

The objective of demonstrating the production of high-purity silicon for long-term, steady-state operation was not attained, although considerable progress was made toward developing an understanding of the deposition mechanisms occurring at high silane concentrations and toward describing the reactor design and operating conditions that enable the production of suitably sized particles at high-throughput rates. This final stage of success will require completion of preliminary experimental efforts to ensure this level of operation. The use of the model developed at Washington University at St. Louis should permit a well-designed experimental program and the basis for the interpretation of data for the design of a commercial unit. With the end of the JPL in-house program, the completion of the development and demonstration of the high potential of the Silane Process that incorporates FBR deposition units will depend upon commercial industrial organizations.

B. SILICON MATERIALS RESEARCH

The JPL Silicon Materials Research Laboratory carried out experimental research involving the effects of impurities on silicon material properties, methods for measuring concentrations of impurity elements in silicon in the ppba range, and techniques for consolidation of the submicrometer silicon powder obtained from the operation of the UCC FSR. Research on impurity effects was done in collaboration with research efforts performed under JPL contracts, especially those with Westinghouse, Monsanto, C.T. Sah Associates, and Northrup Research and Technology Center. Measurements and the development of special measurement procedures were conducted under contracts by Aerospace Corp., the National Bureau of Standards, and Lawrence Livermore Laboratories. These were supplemented by efforts of the in-house program. In the silicon-

powder consolidation work, several apparatuses for melting the fine powder were tried with varying degrees of success.

In support of the Task program dealing with impurity effects, emphasis at JPL was on the determinations of the energy levels and electrical activities associated with specific impurities. The thermally stimulated capacitance (TSCAP) method was used to gather data of emission rates, energy levels, and trap concentrations. A major advantage of the TSCAP measurements and of the closely allied techniques of voltage-stimulated capacitance (VSCAP) and light-stimulated capacitance (LSCAP) is the ability to detect some elements not measurable by other techniques. To secure the data, great care must be taken to:

- (1) Ensure accurate capacitance and temperature measurements.
- (2) Prepare the diodes with special attention paid to methods of preventing surface channel leakage and intersurface irregularity.
- (3) Be especially diligent in the resolution of overlapping signals originating from two closely adjacent trapping levels.

Automated TSCAP and VSCAP techniques were introduced and used to detect electrically active impurity concentrations of as little as 10^{10} atoms/cm³ in a substrate having 10^{14} atoms/cm³ concentration of a primary impurity. These data, along with those obtained under various contracts, formed an information base used to develop an understanding of the major physical mechanisms and chemical reactions involved in the effects of impurities.

Besides analyzing the measurement techniques being developed and the composition data being gathered under the JPL contracts, the effort involving impurity concentration determinations was directed

toward developing procedures and capabilities of the Zeeman atomic absorption spectrometer. This instrument uses the Zeeman effect on a resonant transition to correct automatically for background interference. Trace elements can be measured directly without the need for chemical pretreatments of the samples.

In the course of the study, the commercial HAD Scientific Zeeman Spectrometer was modified, using new designs for the light source and the high temperature furnace. An open-structured instrument had been purchased to permit easy modifications. Also, a technique was developed for sampling submicrometer powder. Preliminary calibration curves were obtained for Cu, Fe, and Cr. Extensive work is needed to establish the capabilities of this instrument and to determine the calibration curves for the diverse elements.

Although the FSR offered the advantages of 100% yield for the conversion of silane-to-silicon, very low energy use, and simple design, the problem remained of devising a method for the consolidation of the submicrometer powder product. Effort was directed to the development of the technique of pedestal melting, in which the powder is introduced into a molten silicon layer on the top of a slowly moving pedestal. There was limited success using small-scale equipment. When this work was terminated, the problem of the formation of slag had yet to be overcome and an optimum heating procedure remained to be established.

In a study by F. Tsay and A. Bauman, transition metal impurities, which had been shown experimentally to act as minority carrier recombination centers in silicon solar cells, were characterized using electron spin resonance (ESR). Impurities were classified into four types based on valence state and electron configuration. A sequence that related to the observed decreasing cell performance caused by impurities was found to be consistent with increased oxidation states of the impurities. A model was developed to explain this correlation.

SECTION VIII

Summary

A. TASK PROGRAM

The responsibility of the Silicon Material Task was to develop processes capable of the large-scale production of polysilicon, suitable for the fabrication of PV solar cells for terrestrial applications, at costs commensurate with a market price \leq \$10/kg (1975 dollars). To provide an information base for evaluating process purification requirements and economics, the program consisted of 11 process developments, of support activities in the areas of chemical engineering, economic analyses, and material characterization, and of investigations of the effects of impurities on the performance of solar cells. Teams of scientists and engineers under contract were involved in activities to develop new processes, to generate chemical and chemical engineering data, to elucidate material composition effects on cell performance characteristics, and to solve a variety of technical problems.

The plan for the process developments contained elements for:

- (1) Demonstration of the technical feasibility of processes through experimental studies using small-scale, primary process reactors.
- (2) Experimental characterization of the operating conditions of scaled-up process units and the assessment of the production and economic potentials of processes.
- (3) Experimental determination of the conditions for steady-state operation of integrated sections of processes (PDUs) with the objectives of performing optimization analyses and process engineering designs.
- (4) Experimental establishment of the operating capabilities of complete processes in EPSDU by obtaining data for steady-state, near-optimum production.
- (5) Operation of large-scale production plants. Several modifications of the Task program and schedule were formulated to meet perceived modified demands for polysilicon production that were calculated from various DOE plans for the PV solar cell industry. The basic program leading to a large-scale production plant in 1986 remained as the guideline, however, until funding restrictions, beginning in FY 81, forced the deletion of the phase for large-scale production plants and limited the scope of the entire program.

B. KEY ACCOMPLISHMENTS

The major success of the Task program was the development of the silane production section of the UCC Silane Process. The culmination was the demonstration of the steady-state, on-stream operation of a 100-MT/year EPSDU and then of the full-scale operation of a 1200-MT/year production plant (which was done under UCC funding). The silane and polysilicon products of this plant have been shown by analyses to be purer than electronic-grade material from conventional Siemens process plants. The silane-to-silicon conversion units in this UCC installation are Siemens-type CVD reactors, which are not capable of the high-throughput, low-energy use operation needed to achieve the low-cost goal of the FSA Project.

Based on the conclusion from a JPL chemical engineering analysis in 1976 that FBR technology should be the primary candidate for development into a low-cost, high-throughput silane-to-silicon conversion reactor, an extensive effort has been directed to this objective. Collaborative R&D programs in the laboratories of JPL and UCC have provided an understanding of the deposition-mechanism and have demonstrated the feasibility of using an FBR at high silane concentrations. At JPL, concentrations of 40 to 60% were usually used. In some runs, the concentrations were 80 and 100%. The conversion efficiency was essentially 100% with a 90% deposition in the bed while limiting the loss of fine particles to less than 10%. The maximum production rate was 3.5 kg/h for a 3-h run for a silane feed concentration of 80%. A product removal rate of 3 kg/h was demonstrated.

The FBR development at UCC was directed toward obtaining the basis for an engineering design. Many long-term runs, ranging up to 80 h, were successfully conducted using silane feed concentrations between 20 and 25%. The deposition efficiency data were approximately the same as obtained at JPL.

To facilitate technology transfer of the silane-FBR technology, a description of the deposition, based on experimental data, was developed at JPL, and a mathematical model for the simulation of the silane-FBR was developed under contract at Washington University at St. Louis.

The technology for the silane-to-silicon FBR has been markedly advanced, removing the prior restrictions of very low silane use and prohibitively high fine-powder formation for silane pyrolysis reactors. Coupled with the highly successful large-scale demonstration of the process for the preparation of very pure silane from metallurgical-grade silicon, the silane-FBR should enable low-cost silicon production to meet the Task goal.

Varying levels of technology maturity were obtained in the other process development contracts of the Task. The most successful of these developments have been advanced further with non-Government funding. These developments are:

- (1) Dichlorosilane-CVD process by HSC. Superior production capabilities for yield, deposition rate, and energy use were demonstrated in the Task program.
- (2) Gas-Phase Sodium Reduction of Silicon Tetrachloride Process by AeroChem Research Laboratories. Continued development programs at AeroChem Research Laboratories and Universal Silicon have resulted in considerable progress toward the demonstration of engineering feasibility.
- (3) Carbothermic Reduction of Silica Process by Dow Corning. Continued developments by Elkem-Exxon, Solarex, and Elkem have led to improvements.
- (4) Sodium-Reduction of Silicon Tetrafluoride by SRI International. Reported material and solar cell data indicate improved product purity.
- (5) Bromosilane Process by J.C. Schumacher. Installation of a pilot plant and design of a production plant were announced by Schumacher.

R&D efforts to develop fully these processes with private funding show evidence of technology transfer from the Task to industry.

Primarily under contracts with Westinghouse Research Center and Professor C.T. Sah, the information, conclusions, and models obtained in the studies of the effects of impurities on solar cell performance have provided the basis for correlations of different solar-grade silicon materials with cell fabrication techniques and with overall economics. These experimental and theoretical results have been used worldwide by groups developing polysilicon processes, by commercial polysilicon producers, and by the solar cell industry.

The main Task program was supported by diverse contractual efforts involving: research laboratories, universities, consultants for reactor research, chemical engineering and economic analyses, impurity concentration measurements, and in-depth process assessments. The JPL group also was active in these technical areas. The information, conclusions, and innovations derived in the Task program have had a worldwide effect on R&D activities and polysilicon production plans.

C. ECONOMICS

Economic analyses were important for evaluation of the potentials of the process developments proposed to achieve the Task cost goal. Independently of the

development contractors, the most intensive analyses were done by C.L. Yaws at Lamar University and later at the Texas Research and Engineering Institute. The results are shown in Table 6. For comparison, the Task goal is \$18.60 (in 1985 dollars).

More mature calculations, reflecting both technical advances that have been made and revisions in line-item costs, are given in Table 7. (The difference in the results are mainly because of the disparate power rates used.)

The most recent UCC estimate (in 1985 dollars) for the conversion of silane-to-silicon by FBRs is based upon the use of four quartz-lined, 12-in.-diameter FBRs in a 1000-MT/year plant. The calculation yielded an incremental product cost of \$6.10/kg of silicon and a price at 30% discounted cash flow of \$10.26/kg silicon. The plant requires a total investment of \$7.2M and an annual operating cost of \$5.53M for the FBR section only.

Table 6. Analyses from Two Final Reports Written by C.L. Yaws, February 1981 and July 1982

Process	Product Cost \$/kg (1985 Dollars)	Sales Price \$/kg (1985 Dollars) 20% ROI
SiH ₄ FSR	12.85	20.08
Zn-SiCl ₄ FBR, Case A*	16.07	25.94
Zn-SiCl ₄ FBR, Case B*	14.72	22.88
SiHCl ₃ -CVD (Siemens)	71.51	—
SiH ₂ Cl ₂ -CVD	30.12	50.27

* Cases A and B differ in the size and number of electrolysis cells.

Table 7. Analyses Presented at FSA Project Workshop on Low-Cost Polysilicon for Terrestrial Photovoltaic Solar Cell Applications, October 1985

Process	Product Cost (1985 Dollars)		Sales Price \$/Kg (1985 Dollars) 20% ROI
SiH ₄ -CVD	24.64 ^a	33.40 ^b	52.33 ^a
SiHCl ₃ -CVD (Siemens)	29.49 ^a	32.20 ^b	55.05 ^a
SiH ₂ Cl ₂ -CVD	19.48 ^a	31.35 ^b	34.82 ^a
SiH ₄ -FBR	—	21.60 ^b	—

^aAnalyses by Professor Carl Yaws, Lamar University.

^bAnalyses by Dr. Y. Shimizu, Osaka Titanium Corp.

To obtain an estimate of the overall product cost, these data were combined with the early economic analysis prepared by Lamar University investigators

(see Section V.D.). The Lamar analysis was modified by the deletion of the costs for the conversion of silane to molten silicon in the process that uses FSRs. A calculation, using the UCC silane-to-silicon FBR data and the modified Lamar analysis, results in estimated overall product costs of \$8.73/kg silicon (1975 dollars) and \$16.05/kg silicon (1985 dollars). The corresponding prices that include a 20% ROI are \$13.66 and \$25.13/kg, respectively. It must be kept in mind that these figures are not exact, but are the most recent preliminary chemical engineering estimates with a range of about $\pm 25\%$.

D. CURRENT STATUS OF POLYSILICON PROCESS TECHNOLOGIES DEVELOPED IN THE TASK

The technology for the conversion of metallurgical-grade silicon to very pure silane in a closed-cycle process, developed under the Task program, has been fully demonstrated by operation by UCC of the Silane Process EPSDU and the 1200-MT/year production plant. The Task goal for low-cost polysilicon, however, cannot be achieved in this plant that uses CVD silane-to-silicon conversion reactors. The experimental database remains to be completed for the engineering design of an FBR that has the required throughput and purity attributes. Continued development of this FBR is underway with corporate funding at UCC.

Other process developments, carried to various levels of maturity in the Task program, showed promise of success and have been continued with private funding. These are the processes developed under contracts with Dow Corning, AeroChem Research Laboratories, SRI International, HSC, and J.C. Schumacher. Descriptions of the technical status of these extended developments remain proprietary, although some information regarding product purity and production plans has been provided.

Efforts for the determination of the effects of impurities on material properties and solar cell performance were conducted primarily by the Westinghouse Research Center and Professor C.T. Sah of the University of Illinois. These efforts provided an extensive information and model basis usable for calculations and analyses. These have been valuable to polysilicon process developers, polysilicon producers, and solar cell manufacturers. Recent studies by other groups dealing with the effects of impurities on high-efficiency cells have extended this work.

E. TECHNOLOGY REQUIRED TO ACHIEVE THE TASK GOAL

Consideration of the technology required to achieve the Task goal is limited to the UCC Silane Process. For this process, development must be completed of a silane-to-silicon FBR that has the high-throughput capacity necessary to render the Silane Process capable of meeting the Task goal. Although considerable progress has been made by extensive studies in the JPL and UCC laboratories, several technical objectives must be achieved to obtain an engineering design for an FBR capable of long-term, steady-state, high-volume operation producing semiconductor-grade silicon granules. The most difficult objective is the establishment of product purity. Efficiency must be demonstrated of a reactor material or a reactor liner that can prevent the contamination of both seed particles and product. Capability for long-term, steady-state, high-throughput operation, while yielding pure polysilicon, also remains to be firmly established. The Task goal will be achieved when an analysis of the data for the operation of an integrated silane-FBR process shows the ability to produce suitably pure polysilicon at a product cost commensurate with the Task price objective.

APPENDIX A

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APPENDIX B

Glossary

AM0	air mass zero	JPL	Jet Propulsion Laboratory
BSF	back-surface field	LAPP	Low-Altitude Plume Program
Caltech	California Institute of Technology	LSCAP	light-stimulated capacitance (method)
CFP	continuous-flow pyrolyzer	LSSA	Low-Cost Silicon Solar Array (Project)
CSTR	continuous stirred-tank reactor	mgSi	metallurgical-grade silicon
CVD	chemical vapor deposition	MIT	Massachusetts Institute of Technology
Cz	Czochralski	NAA	neutron activation analysis
DCF	discounted cash flow	PCD	photoconductivity decay
DOE	U.S. Department of Energy	PDU	process development unit
EPSDU	experimental process system development unit	PSDF	Process System Development Facility
ERDA	Energy Research and Development Administration	PV	photovoltaic(s)
ESR	electron spin resonance	R&D	research and development
FBBR	fluidized bubbling-bed reactor	ROI	return on investment
FBR	fluidized-bed reactor	SEM	scanning electron microscope
FSA	Flat-Plate Solar Array (Project)	SMSR	silane-to-molten silicon reactor
FSR	free-space reactor	SRI	Stanford Research Institute
FZ	float-zone	SSPC	steady-state photoconductivity
HSC	Hemlock Semiconductor Corp.	TSCAP	thermally stimulated capacitance (method)
HTFFR	high-temperature, fast-flow reactor	UCC	Union Carbide Corp.
ID	inside diameter	V_{oc}	open-circuit voltage
I_{sc}	short-circuit current	VSCAP	voltage-stimulated capacitance (method)
		WBS	work-breakdown structure

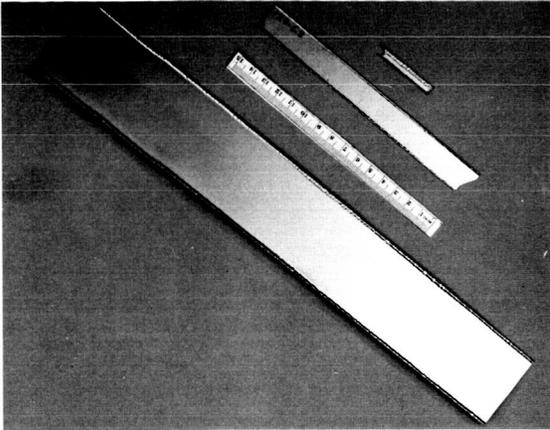
Prepared by the Jet Propulsion Laboratory, California Institute of Technology,
for the U.S. Department of Energy through an agreement with the National
Aeronautics and Space Administration.

The JPL Flat-Plate Solar Array Project is sponsored by the U.S. Department of
Energy and is part of the National Photovoltaics Program to initiate a major
effort toward the development of cost-competitive solar arrays.

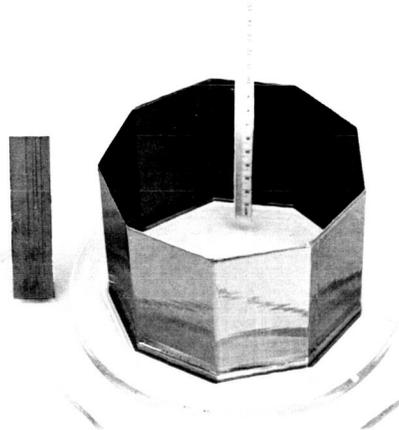
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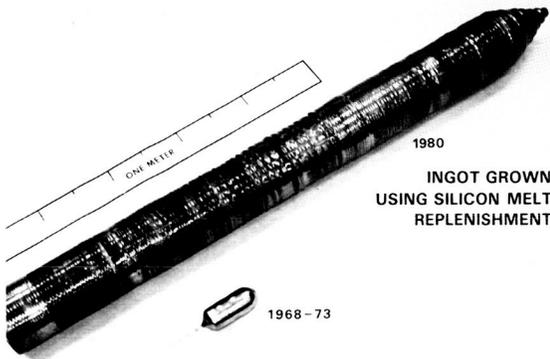
More Technology Advancements



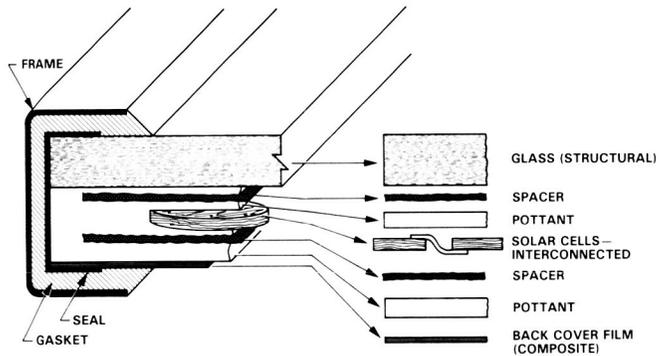
Dendritic web silicon ribbons are grown to solar-cell thickness. Progress is shown by experimental ribbons grown in 1976 and 1978 and a ribbon grown in a Westinghouse Electric Corporation pilot plant.



The edge-defined film-fed growth silicon ribbons are grown to solar-cell thickness. A DOE/FSA-sponsored research ribbon grown in 1976 is shown next to a nine-sided ribbon grown in a Mobil Solar Energy Corporation funded configuration.



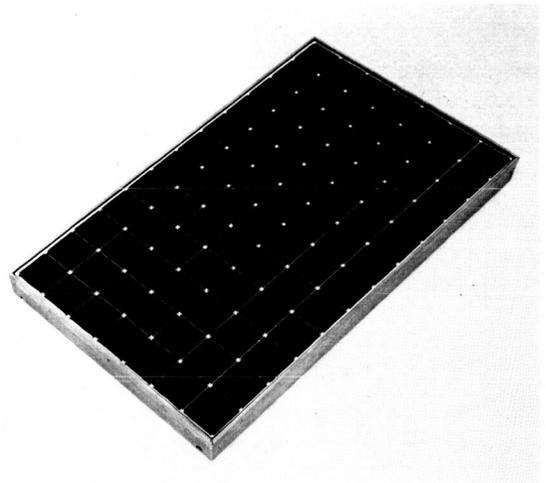
Czochralski silicon crystals as grown are sawed into thin circular wafers. (Support for this effort was completed in 1981.)



Typical superstrate module design is shown with the electrically interconnected solar cells embedded in a laminate that is structurally supported by glass. Materials and processes suitable for mass production have been developed using this laminated design.



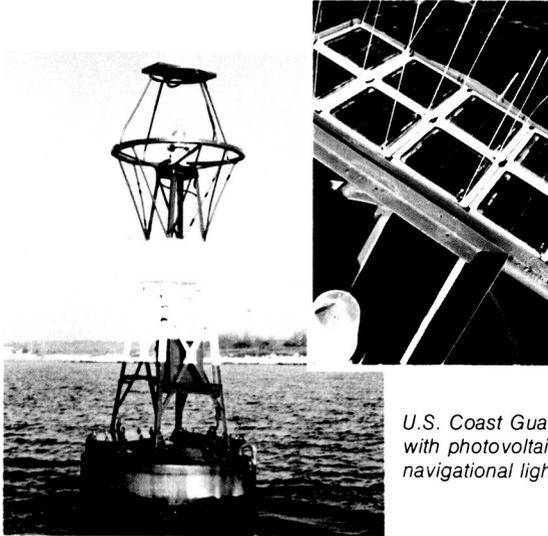
Prototype modules have passed UL 790 Class A burning brand tests which are more severe than this spread of flame test.



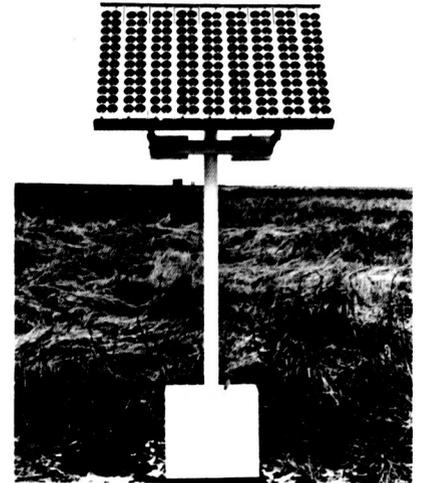
A 15.2% efficiency prototype module (21 x 36 in.) was made by Spire Corp. using float-zone silicon wafers. Recently, similarly efficient modules were fabricated from Czochralski silicon wafers.

Photovoltaic Applications

1975



U.S. Coast Guard buoy with photovoltaic-powered navigational light.



Photovoltaic-powered corrosion protection of underground pipes and wells.

Later...



House in Carlisle, Massachusetts, with a 7.3-kW photovoltaic rooftop array. Excess photovoltaic-generated power is sold to the utility. Power is automatically supplied by the utility as needed.



A 28-kW array of solar cells for crop irrigation during summer, and crop drying during winter (a DOE/University of Nebraska cooperative project).

1985



1.2 MW of photovoltaic peaking-power generation capacity for the Sacramento Municipal Utility District. (The 8 x 16 ft panels are mounted on a north-south axis for tracking the sun.)