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Flat-Plate
Solar Array Project

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A Review of the Silicon Material Task

R. Lutwack

February 1, 1984

Prepared for
U.S. Department of Energy
Through an Agreement with
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ABSTRACT

The Silicon Material Task of the Flat-Plate Solar Array Project was assigned the objective of developing the technology for low-cost processes for producing polysilicon suitable for terrestrial solar-cell applications. The Task program comprised sections for process developments for semiconductor-grade and solar-cell-grade products. To provide information for deciding upon process designs, extensive investigations of the effects of impurities on material properties and the performance of cells were conducted. The silane process of the Union Carbide Corp. was caried through several stages of technical and engineering development; a pilot plant was the culmination of this effort. The work to establish silane fluidized-bed technology for a low-cost process is continuing. The advantages of the use of dichlorosilane in a Siemens-type process were shown by Hemlock Semiconductor Corp. The development of other processes is described.

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FOREWORD

The Silicon Material Task of the Jet Propulsion Laboratory (JPL) Flat-Plate Solar Array Project (FSA), initially titled the Low-Cost Silicon Solar Array Project, was assigned to develop the technology for processes capable of producing polycrystalline silicon (Si) suitable for terrestrial applications at a price lower than $14/kg (1980 $). Contractual efforts were conducted to develop processes yielding semiconductor-grade or solar-cell-grade Si products. Studies of the influence of impurities on Si material properties and cell performance were performed to determine the concentration levels of specific elements commensurate with various degrees of cell-efficiency degradation. Supporting efforts included measuring impurity concentrations, fabricating and measuring cell characteristics, theoretical and experimental studies of chemical engineering and photovoltaic problems, and economic analyses. Eleven candidate processes were investigated; development was carried to various levels of maturity. During the program process developments were eliminated because of failure to demonstrate technical feasibility, the need to reduce the number of candidates at preset milestones of the Task program, or the restrictious of Task budgets.

Only the silane process of Union Carbide Corp. (UCC) progressed into the phase equivalent to a pilot plant, an Experimental Process System Development Unit (EPSDU). The completion of the EPSDU, after the design and purchase of the equipment and the partial installation at East Chicago, Indiana, was prevented by a severe reduction in the budget. Under an agreement between UCC and the Department of Energy (DOE), the EPSDU has been relocated in Washougal, Washington, and the operation data will be reported to JPL. These data will be analyzed to assess the capabilities of this process for product purity, production capacity, steady-state production characteristics, and product cost in the context of a 1000 MT/yr plant. Economic analyses, based on the use of a free-space reactor Si deposition unit, gave a preliminary product price of about $13/kg in 1980 $ and at 15% discounted cash flow (DCF).

The dichlorosilane chemical vapor deposition (CVD) process of Hemlock Semiconductor Corp. is the other development remaining in the Task program. In this process the modification of the well-defined technology for CVD in a Siemens reactor is combined with the technology from the UCC process for the conversion of metallurgical-grade Si to dichlorosilane. There is a high probability of success in demonstrating the practicality of this process. A Process Development Unit (PDU) incorporating a redistribution system and a deposition reactor has been used for the studies. Economic analyses range from about $25 to $34/kg (1980 $ at 10% DCF), the variations being due to different assumptions for the costs of energy use, deposition reactors, and buildings.

The elements used in the studies of the effects of impurities on solar-cell performance were those present in metallurgical-grade Si and those believed likely to be adventitiously introduced during polycrystalline Si production and single-crystal growth. The tolerable concentrations were found to be determined by the effects of specific metallic impurities on the performance of cells, the effects of boron (B) and phosphorus (P) on resistivity and single-crystal yield in ingot growth, and the effects of total impurity concentration in the Si feedstock on single-crystal growth yield. The effects of impurities on cell efficiency were related empirically through the base diffusion length and were shown to be species-dependent; the concentrations causing a 10% decrease in efficiency ranged from 0.1 ppba for tantalum to 10 ppma for copper, for example. The tolerable concentrations in the polycrystalline Si are dependent on the methods used for ingot or sheet processing. The limits can be relaxed considerably for a near-equilibrium, unidirectional solidification in which liquid-solid impurity segregation is the concentration controlling factor. The upper limit of tolerable B concentration is set by the lowest resistivity to be used in the cell manufacture (p-base); a resistivity of 0.3 ± 0.1 ohm-cm gives an upper limit of B concentration of 2 ppma in the polycrystalline Si. The yield of usable single-crystal ingot is limited, however, if the Si is compensated; P concentration must be <0.5 ppma if the single-crystal yield is to be 90% for 0.3 ohm-cm Si and five melt replenishments using the Czochralski method, for example. Crystal structure breakdown occurs when the total impurity concentration exceeds a critical value for a particular set of conditions of ingot diameter and growth rate. The critical concentration is in the range of 200 to 500 ppma when a 10-cm-dia Czochralski crystal is pulled at a rate of about 8 cm/hour, for example. Various trade-offs must be made in the structuring of a process sequence from polycrystalline Si through the fabrication of photovoltaic cells. The available data base for these trade-off studies has been incorporated into a slide rule.

In a fundamental approach to the impurity effects problem a transmission-line-equivalent circuit model was developed to compute the exact steady-state characteristics of one-dimensional Si solar cells. The model was used for calculations of limiting concentrations of specific impurities for defined cell structures and efficiency. A model was also developed to study the effects of defects across the back-surface-field junction on the performance of high-efficiency cells. A new theory to distinguish an acceptor-like deep level from a donor-like deep level was developed using measured values of the thermal emission and capture cross sections. This theory also provides information concerning the lattice distortion around an impurity atom before and after the capture or emission of an electron or hole at the impurity center.

Portions of the Silicon Material Task program are still active under other FSA Tasks. Parts of the process developments under the contracts with UCC and Hemlock are under way; an engineering development of the silane fluidized-bed reactor (FBR) is being carried out by UCC; a basic investigation of the technology for a silane FBR is being done by JPL; research to characterize the aerosol phenomena and to increase the size of particles forming by the thermal decomposition of silane is being performed at the California Institute of Technology, and fundamental studies for models of high-efficiency solar cells by Professor C.T. Sah are continuing.

ACKNOWLEDGMENTS

Authorities in the fields of chemical engineering and solid-state physics were used throughout the Task program as consultants to provide critiques, to participate in critical technology reviews, and to address important technical problems. In the area of chemical engineering the following were consultants: Dr. Donald Bailey, Traverse City, Michigan; Dr. Thomas Fitzgerald, Rossmoor, California; Professor S. Friedlander, University of California at Los Angeles; Professor O. Levenspiel, Oregon State University, and Professor C. Yaws, Lamar University. Professor C.T. Sah was the consultant in the area of solid-state physics.

The efforts of JPL staff members were involved in laboratory research, technology critiques, process and problem analyses, and the technical management of contracts. The following engineers contributed to the Task program: P. Berman, A. Briglio, E. Cleland, R. Cockrum, C. Coulbert, R. Hogle, G. Hsu, R. Josephs, H. Levin, A. Praturi, R. Rhein, N. Rohatgi, A. Salama, P. Seshan, and A. Yamakawa.

The following technicians contributed to the program: A. Allen, J. Andrews, J. Bell, D. Feller, L. Ford, D. Huls, J. Lloyd, and O. McCullough.

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which were, therefore, high risks for commercialization. It was intended that the experimental operation of an EPSDU would provide the opportunities to correct design errors; to determine the consumption of utilities and the suitability of waste-disposal measures; to establish practical steady-state operating procedures and production conditions; to obtain data for optimization calculations, and to evaluate the requirements for instrumentation, controls, and on-line analyses more realistically. Later, if necessary, the EPSDU could be operated concurrently with a large-scale plant to aid in solving operation problems and to continue studies for process optimization.

The initial Task program and schedule were formulated to meet the Project schedule for full-scale production plants to be on line in 1986. This very ambitious schedule was considered to be appropriate for the more mature process development candidates, i.e., those for which the chemistry and some of the chemical engineering had been done before a contract start in the Task program. The less mature process developments were placed on different schedules. Technology problems, changes in technical direction and project goals, and increasingly limited budgets caused modifications in each contract schedule.

The process developments had been divided into two sections at the start of the program: those for preparing a semiconductor-grade Si and those for a solar-cell-grade Si. The first category was the more easily defined, since the product Si was to be equivalent to the Si generally acceptable to the semiconductor industry. Solar-cell-grade Si was defined in a simplistic way as a material sufficiently pure to be processed into cells with 12% AM1 efficiency, assuming that the single-crystalline materials for the cell fabrication would be obtained from the polycrystalline Si by a near-equilibrium solidification procedure, such as the Czochralski technique. Each of the process developments was categorized at the start of the contracts, the classifications being based on assessments of the partial purification capabilities of the processes; those involving gaseous intermediates that were purified by distillation were assigned the goal of producing semiconductor-grade Si. It was understood that classification changes might be made later, since process compromises might force the selection of reaction conditions and materials of construction such that additional impurities would be introduced. This might result in higher concentrations than the acceptable limits for semiconductor-grade Si. It was also recognized that changes would be necessary as a consequence of the results of the experimental and theoretical studies of impurity effects, which were intended to provide a quantititive model for selecting the purity requirements.

The Task effort for the study of the effects of impurities on the properties of Si material and solar cells consisted of two phases: (1) measurements of the effects of impurities that are present in metallurgical-grade Si or that might be introduced adventitiously by a reaction step of one of the processes being studied, and (2) the determination of the interrelationships of impurities and material processing steps and their combined effects on material and solar-cell characteristics. The results of these investigations were intended to be used to define solar-grade Si and to serve as guidelines for determining the purification requirements for various processes.

The main Task program was supported by contracts with research laboratories, universities, and consultants for chemical engineering and economic analyses of the candidate processes; for reactor research; for research of impurity concentration measurement techniques; for analyses of technical problems arising in the process development programs; and for in-depth assessments of process technologies. In addition, the JPL engineering staff conducted theoretical and experimental studies and performed technical assessments of the technological progress of all the contractual efforts.

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SECTION II

SUMMARIES OF TASK PROGRAMS

A. PROCESS DEVELOPMENTS FOR SEMICONDUCTOR-GRADE SILICON

1. Dichlorosilane Chemical Vapor Deposition Process (Hemlock Semiconductor Corp., JPL Contract No. 955533)

Dichlorosilane (SiH_2Cl_2) chemical vapor deposition (CVD) can be considered as a two-step process in which the first step is the generation of SiH_2Cl_2 in a processing sequence that is patterned after the steps in the Union Carbide Corp. (UCC) silane process for the hydrochlorination of metallurgical-grade Si (mgSi) and the disproportionation of trichlorosilane ($SiHCl_3$) to SiH_2Cl_2. The dispropotionation step differs from that of the silane process in that here a Dow Corning Corp. amine catalyst is used for the disproportionation reaction. The second step is the reduction of SiH_2Cl_2 by H_2 in a modified Siemens deposition reactor. The process concept is based on the reasoning that the use of SiH_2Cl_2 in a Siemens reactor would be advantageous when compared with $SiHCl_3$ due to its greater deposition rate and more favorable conversion yield per pass.

As in the silane process, the processing sequence of the first stage consists of steps for the production of $SiHCl_3$ from the hydrochlorination reaction of H_2 and silicon tetrachloride ($SiCl_4$) with mgSi in a fluidized-bed reactor (FBR); the purification of the $SiHCl_3$ by the removal of metals as chlorides and of high-volatility gases and then of the residual $SiCl_4$ by distillation; and the disproportionation of $SiHCl_3$ into SiH_2Cl_2 and $SiCl_4$ and the purification of the SiH_2Cl_2 by distillation. In the second stage, Si is produced from the high-temperature H_2 reduction of SiH_2Cl_2 by deposition onto heated filaments in a Siemens-type reactor.

The primary overall chemical reactions are:

(1) Hydrochlorination of mgSi:

$$Si + 2H_2 + 3SiCl_4 \underset{Cu}{=} 4SiHCl_3 \text{ at } 500^\circ C \text{ and } 515 \text{ lb/in.}^2$$

(2) Disproportionation reaction:

$$2SiHCl_3 \underset{\text{Dowex MWA-1}^*}{=} SiH_2Cl_2 + SiCl_4 \text{ at } 80^\circ C$$

(3) Si deposition reaction:

$$SiH_2Cl_2 = Si + HCl + \text{chlorosilane mixture at } 1050^\circ C$$

The $SiCl_4$ in the product streams from these reactions is recycled, as is the H_2 recovered from the product stream of the hydrochlorination reactor and from the Siemens-type reactor. This recycling improves upon the advantages

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*Trademark of Dow Corning Corp.

of deposition rate and yield by obviating dealing with a large amount of byproduct $SiCl_4$. The greater deposition rate and yield characteristics, together with reactor improvements, also lead to the potential for a large decrease in 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 $SiHCl_3 \longrightarrow SiH_2Cl_2$ redistribution reaction and the characteristics of catalysts, and to do a preliminary engineering design of an EPSDU.

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. Optimized operating conditions were derived from the results. In a series of runs it was shown that the redistribution reactor could be run 95% on line; 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; no vapor-phase nucleation, and hence no fine powder formation, occurred; the product was of semiconductor-grade purity, and the rod surface was acceptably dense and coherent. The Si was further characterized by evaluating solar cells processed from it; the cell efficiencies were as good as baseline cells from $SiHCl_3$ Siemens Si and were in the range of 12% to 14% (cells were made and tested by the Westinghouse Research Center).

A major problem arose during the chemical and physical characterization of the 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 for diluting the SiH_2Cl_2 immediately (in the exit stream from the SiH_2Cl_2 distillation column) with H_2. Thus there is to be no SiH_2Cl_2 storage.

An economic analysis for a 1000-MT/yr plant based on a preliminary engineering process design indicated a price of $24/kg in 1980 $ and at 20% return on investment (ROI). The development continues with a program for obtaining further data for the full descriptions of the separate reactors and of a PDU comprising the redistribution system and the CVD reactor.

2. Bromosilane Process
(J.C. Schumacher Co., JPL Contract No. 954914)

The feasibility of using a bromosilane chemical system for the production of polycrystalline Si was examined in this effort. The apparent advantages of the $SiHBr_3$ system over the $SiHCl_3$ system are the capability of operating at lower temperatures without causing homogeneous nucleation and the formation of fine powders; a decreased tendency for wall deposition and polymer formation; an increased reaction rate for the H_2 reduction of bromosilanes; and better partition coefficients for purification across the liquid-vapor phase boundary. The recognizable disadvantage is the raw material cost, but this would be greatly reduced for a closed-cycle process.

The primary overall chemical reactions are:

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

$3SiBr_4 + Si + 2H_2 = 4SiHBr_3$ at 650°C

(2) Si production:

(a) Thermal decomposition:

$4SiHBr_3 = 3SiBr_4 + Si + 2H_2$ at 850°C

(b) H_2 reduction:

$SiHBr_3 + H_2 = Si + HBr +$ bromosilane mixture at 1000°C

A major initial task was to investigate the behavior of a high-velocity gas-phase reaction for the H_2 reduction of bromosilanes. A continuous-flow reactor into which Si seed particles were introduced to be mixed with and conveyed by high-velocity gaseous reactants through the reaction zone was proposed after a chemical engineering analysis. However, early experiments, directed toward obtaining overall yield data and to characterizing fully the kinetics and thermodynamics of this reaction system, indicated the need for increased residence time and greater deposition substrate particle packing density. Hence, a changeover to an FBR was made.

Limited experiments in the H_2 reduction of $SiHBr_3$ in an FBR gave a 60% yield at 1000°C. Analogous to the chlorosilane system, the major byproduct is $SiBr_4$. Analyses of designs for processes incorporating an FBR for the deposition reactor and a hydrobromination reactor to generate the $SiHBr_3$ were performed. These indicated that the Task goal could be reached using either hydrogen reduction or thermal decomposition of $SiHBr_3$. Preliminary optimization calculations did not show distinct advantages for either path. Budget restrictions and Project schedule commitments forced termination of the work at this point.

3. Silane Process
(Union Carbide Corp., JPL Contract No. 954334)

The silane process being developed by UCC can be perceived as a two-step process. In the first step, mgSi is transformed into extremely pure silane (SiH_4); in the second step, the SiH_4 is thermally decomposed to yield Si. The feedstock of mgSi and some makeup chlorine in the form of silicon tetrachloride ($SiCl_4$) are the only chemicals introduced into the closed system. The main byproducts of the chemical conversion, intermediate purification, and deposition process steps are hydrogen (H_2) and $SiCl_4$; these are recycled. The metal impurities are removed as chlorides.

The processing sequence consists of the following steps: (1) the production of trichlorosilane ($SiHCl_3$) from the hydrochlorination reaction of H_2 and $SiCl_4$ with mgSi in an FBR; (2) the purification of the $SiHCl_3$ by the removal of metals as chlorides and of high-volatility gases, and then of the residual $SiCl_4$ by distillation; (3) the disproportionation of $SiHCl_3$ into dichlorosilane (SiH_2Cl_2) and $SiCl_4$; (4) the purification of the SiH_2Cl_2; (5) the disproportionation of the SiH_2Cl_2 into SiH_4 and $SiHCl_3$; (6) the purification of SiH_4 by distillation; and (7) the thermal decomposition of SiH_4 to yield Si.

The primary overall chemical reactions are:

(1) Hydrochlorination of mgSi:

$$Si + 2H_2 + 3SiCl_4 \underset{Cu}{=} 4SiHCl_3 \text{ at } 500^{\circ}C \text{ and } 515 \text{ lb/in.}^2$$

(2) Disproportionation reaction 1:

$$2SiHCl_3 \underset{\text{Amberlyst } 21^*}{=} SiH_2Cl_2 + SiCl_4 \text{ at } 70^{\circ}C$$

(3) Disproportionation reaction 2:

$$3SiH_2Cl_2 \underset{\text{Amberlyst } 21^*}{=} SiH_4 + 2SiHCl_3 \text{ at } 70^{\circ}C$$

(4) Thermal decomposition:

$$SiH_4 \longrightarrow Si + 2H_2 \text{ at about } 700^{\circ}C$$

The $SiCl_4$ in the product streams from these reactions is recycled, as is the H_2 recovered from the SiH_4 decomposition and from the product stream of the hydrochlorination reactor. (The chemistry of the hydrochlorination and disproportionation reactions had been studied by UCC before the start of the JPL contract.)

The engineering feasibility of the process was proven in Phase I by: (1) operating a PDU for the conversion of $SiHCl_3$ to SiH_4; (2) determining the conditions for the closed-cycle production of SiH_4 from mgSi by incorporating a hydrochlorination reactor in the PDU; (3) obtaining extensive data for the reaction chemistry, kinetics, chemical properties, and thermodynamics to support the process development efforts; (4) showing experimentally that a free-space reactor could be used for the conversion of SiH_4 to Si; and (5) providing experimental evidence that fluidized-bed reactor technology for the deposition of Si on seed particles was an alternative.

Phase II was the process-design phase. A complete and technologically simple process flow sheet to be used as a basis for design and costing was produced from engineering process-design studies. A detailed process-design package was prepared for an EPSDU, which was sized at 100 MT/yr (the EPSDU is equivalent to a pilot plant). To generate an overview for a production and cost analysis, a functional process design for a 1000 MT/yr plant was prepared. In this cost analysis the plant cost was found to be \$8.8 million, and the product price, calculated for 15% discounted cash flow (DCF), was \$9.50/kg (1980 \$) for a molten Si product. Extension of the calculation to a process incorporating

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*Trademark of Rohm and Haas Corp.

an FBR to produce a granular solid product (albeit very premature, since a substantial development of the FBR remained to be done) led to a conclusion that the cost of incorporating this deposition reactor into the process would add about \$1/kg to the product price of SiH_4. The technology and economic bases for the Phase III EPSDU program were established in Phase II.

Phase III involved the design, installation, operation, and evaluation of the EPSDU and the continuation of a R&D task for the deposition reactor. A complex, detailed work breakdown structure was used to describe, coordinate, and track the Phase III EPSDU activities. Reaction data for the optimization of the hydrochlorination reactor were obtained under contracts with the Massachusetts Institute of Technology and Solarelectronics Corp. An extensive effort in the design, specification, and fabrication or procurement of equipment was made. The installation of the EPSDU was begun in East Chicago, Indiana. However, full support of the EPSDU by DOE became impossible in mid-1981, due to severe budget restrictions. As a consequence, the contract was modified to allow the title to the EPSDU equipment to be transferred to UCC, requiring in return an obligation by UCC to complete the installation, to operate the EPSDU experimentally, and to provide to JPL all design and operation data obtained for the silane section. The data for the SiH_4-to-Si conversion will not be provided, since a proprietary (Komatsu Electronics Ltd.) deposition reactor will be used. Under this agreement, the EPSDU was dismantled at East Chicago, Indiana, and reinstalled at a UCC site in Washougal, Washington.

The data for steady-state operation of the EPSDU and the subsequent optimization of operating conditions will provide the basis for the design of a 1000 MT/yr plant. Although the incorporation of the Komatsu (Siemens-type) deposition reactors will enable production costs lower than current industry values, the JPL-DOE goal of less than \$14/kg (1980 \$) market price will not be achieved by a silane process incorporating this reactor; it can only be reached by the use of a different deposition reactor, such as the FBR.

The technology for a SiH_4 FBR is being developed by UCC under a JPL contract. In a complementary effort, a more basic FBR research program is under way at JPL. The objective of the UCC work is to develop a description of the operating requirements and characteristics for steady-state operation at a SiH_4 concentration limited to about 25% in H_2. Early results indicate that the FBR is capable of high throughput at low cost.

B. PROCESS DEVELOPMENTS FOR SOLAR-CELL-GRADE SILICON

1. Synthesis of Silane and Silicon in a Nonequilibrium Plasma Jet (AeroChem Research Laboratories, Inc., JPL Contract No. 954560)

The original objective of this program was to determine the feasibility of the high-volume, low-cost production of high-purity silane (SiH_4) or solar-cell-grade Si from chlorosilanes and H_2 using a nonequilibrium plasma jet. The emphasis was changed near the end of the program to determine the feasibility of preparing amorphous Si films directly for photovoltaic devices using this method. The nonequilibrium plasma jet was produced by partially dissociating H_2 to hydrogen atoms in a 50-torr to 100-torr glow discharge and expanding the H/H_2 mixture through a nozzle. A high flux density of hydrogen atoms is thus produced at concentrations of about 3 mol % with about 30% energy-utilization efficiency. The jet was then mixed with $SiCl_4$, and the reaction proceeded at temperatures of 400° to 600°K.

One of the suggested reaction paths was: $SiCl_4 + H \rightarrow SiCl_3 + HCl$, $SiCl_3 + H \rightarrow SiCl_2 + HCl$, $SiCl_2 + H_2 \rightarrow SiH_2Cl_2$, $SiCl_2H_2 + H \rightarrow SiClH_2 + HCl$, $SiClH_2 + H \rightarrow SiH_2 + HCl$, $SiH_2 + H_2 \rightarrow SiH_4$. Yields of SiH_4, $SiHCl_3$, or SiH_2Cl_2 were found to be too low to be economically attractive. However, both amorphous and polycrystalline silicon films that adhered strongly to Pyrex, Vycor, aluminum, or carbon were prepared with either $SiCl_4$ or $SiHCl_3$ reactants. Strongly adhering films using SiH_4 were more difficult to prepare. Doping such films with phosphorus by adding phosphine reduced their electrical resistivity by two orders of magnitude. The conclusion was that the nonequilibrium plasma jet should be evaluated further as a highly efficient technique for producing amorphous silicon films for photovoltaic cells. However, no R&D program for this purpose ensued, as a consequence of a Project program decision.

2. Silicon Halide--Alkali Metal Flames As a Source of Solar-Grade Silicon

(AeroChem Research Laboratories, Inc., JPL Contract No. 954777)

The feasibility of using continuous, high-temperature flame reactions of alkali metals and Si halides to produce solar-grade Si was investigated. From equilibria calculations it was shown that there are ranges of operating conditions in which Si can be produced in a condensed phase, with the alkali-metal salt byproduct as a vapor. The vapor-phase reaction of sodium (Na) with $SiCl_4$ was proposed as the primary step of a process. The chemical reaction is:

$$4Na + SiCl_4 \xrightarrow{1475^{\circ}C} Si + 4NaCl.$$

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

(1) The reactions of gaseous Na or potassium (K) with $SiCl_4$ or $SiHCl_3$ produce stable high-temperature flames characterized by rapid kinetics and yield free Si.

(2) Flames of gaseous Na or K with silicon tetrafluoride are characterized by much lower temperatures and slower kinetics; free Si is produced only if the reactor is hotter than about 1000°K, so that formation of sodium fluorosilicate is prevented. Additional heat input would be necessary to separate the product Si from the sodium fluoride in the gaseous phase.

(3) The Si produced from the Na/SiCl4 reaction can be separated from the byproduct NaCl(g) if the reactor temperature is above $\approx$1750°K and the inert gas (argon) in the system is minimized.

(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 $T \leq 1200^{o}K$, causing severe material problems. Similar problems are observed with pyrolytic graphite or coated graphite. At $T \geq 1700^{o}K$ these problems are not observed with graphite, although the coatings still fail.

It was recommended that the Na-$SiCl_4$ reaction system be evaluated further as a process for producing solar-grade Si.

3. Sodium Reduction of Silicon Tetrachloride in an Impaction Reactor (AeroChem Research Laboratories, Inc., JPL Contract No. 955491)

The feasibility of using continuous high-temperature flames of the rapid, exothermic reaction of Na with $SiCl_4$ to produce low-cost, solar-grade Si was investigated further. Studies were performed 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 of reactor construction, and to make preliminary engineering and economic analyses of a scaled-up process. An impaction technique was used for Si collection, and the feasibility of making and collecting Si was demonstrated. In the final one-hour runs, Si ingots weighing about 250 g were routinely produced, with separation collection efficiencies of about 80%. The longest runs of 1 1/2 hours were limited by reactant reservoir capacity and not by design or equipment problems. Metal impurity levels were in the 1 to 10 ppma 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 Si, alumina, or silicon carbide for the collector, were shown to be satisfactory materials of construction.

A preliminary process design for a 1000 MT/yr plant led to a calculation of a product cost estimate of about $10/kg (1980 $).

A Project program decision forced by budget considerations caused the termination of the research on this process.

4. Zinc Reduction of Silicon Tetrachloride (Battelle Columbus Laboratories, Ohio, JPL Contract No. 954339)

Thermodynamic and chemical engineering analyses of several processes for the preparation of Si were performed as the first step of this program. The processes included the zinc (Zn) reduction of $SiCl_4$ in an FBR to yield a granular product, and several versions of the thermal decomposition or H_2 reduction of silicon tetraiodide (SiI_4). Only a process involving the Zn-$SiCl_4$ reaction was shown to be capable of achieving the Task goal.

The primary chemical reactions for this process are:

(1) Si production:

$2Zn + SiCl_4 = 2ZnCl_2 + Si$ at 920°C

(2) Zn regeneration:

$ZnCl_2 = Zn + Cl_2$ by electrolysis

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

A miniplant, consisting of a 5-cm-dia 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 rapidly decreasing conversion efficiency (a change of 0.1%/°C from a 72% thermodynamic value at 927°C for a stoichiometric mixture). Use of a graded bed-temperature was shown to increase the conversion efficiency over that obtained in an isothermal bed. Other aspects of the process, such as the condensation and fused-salt electrolysis of the $ZnCl_2$ byproduct for recycling of Zn and Cl_2, were studied to provide information required for the design of a 50 MT/yr experimental facility, visualized as the next stage of development. The purity of the product was determined in an ancillary study in which the granular product Si was treated thermally by the Westinghouse Research Center to remove residual Zn; 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, which consisted of four major units of the process (Zn vaporizer, $ZnCl_2$ condenser, FBR, and $ZnCl_2$ electrolysis cell), sized at 50 MT/yr, was designed and installed. A series of operating and design problems was encountered in the attempts to perform experiments with this integrated unit. As a consequence of the experiments, improvements in the design and operation of these units were undertaken and their experimental limitations were partially established. More extensive redesigns of the equipment were prevented by budget restrictions, and the performance characteristics of the PDU were not determined.

Projected Si costs of $10.29 and $12.19 per kg (1980 $) for a 1000-MT/yr facility were calculated, the range depending upon the number and size of the FBRs and $ZnCl_2$ electrolytic cells used; an energy payback time of 5.9 months was also calculated.

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

5. Direct-Arc Furnace Process
(Dow Corning Corp., JPL Contract No. 954559)

Development of this two-step process for the preparation of solar-grade Si incorporated as its first step the carbothermic reduction of quartz in a direct-arc furnace; this is the basis of the commercial process for producing metallurgical-grade Si. In this effort, the concept was to use extremely pure quartz and carbon reductants and to control the conditions of the furnace carefully. The second step was to be a unidirectional solidification procedure, like the Czochralski technique for the preparation of single crystal ingots; in this manner, a considerable degree of purification would take place due to the rejection of impurities in the liquid Si following the limits of the near-equilibrium liquid-solid distribution coefficients.

As a first step, an intensive survey of materials usable as reactants was made; the criteria were price, chemical activity, and purity. The purest quartz available in the United States and Canada was used. 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 Si were prepared in 60-hour runs at a maximum rate of 3 kg/h.

The impurity concentrations in the products, measured by emission spectroscopy, were found to be less than 10 ppmw for each of the elements measured with the exception of aluminum (Al) and iron (Fe), which were in the range of 50 to 100 ppmw. Attempts to attain further purification by vacuum evaporation were unsuccessful. The second-step purification by Czochralski crystal growth gave Si with impurity concentrations below the limits established for this contract with the exception of Al (1 ppma), boron (B) (7 ppma), and phosphorus (P) (0.5 ppma).

The inability to achieve the concentration goals set for B and P was the most formidable barrier for this process, since, in effect, these goals were based on the objective of obtaining economically acceptable yields of single-crystal ingots (by the Czochralski technique) that were within specified resistivity limits. Thus, the process was finally effectively judged by the concentrations of B and P. (In one case, a single-crystal ingot produced from a second Czochralski pull was fabricated into solar cells; these cells had AM1 efficiencies ranging from 8.2% to 14%, AR coated.)

An energy analysis of the two-step process indicated a five-month payback time. A product cost of $12 (1980 $) was estimated for a 3000 MT/yr plant. Further process development 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 was recommended by Dow Corning. This program was terminated, due to an inability to demonstrate the capability of reaching all of the concentration goals and to Task budget restrictions.

6. Silicon Difluoride Transport Process
(Motorola Inc., JPL Contract No. 954442)

This work was intended to develop a process in which the primary step is a temperature-gradient purification reaction, the mgSi feedstock being converted into the intermediate silicon difluoride (SiF_2) by reaction with silicon tetrafluoride (SiF_4). In subsequent process steps the SiF_2 becomes polymerized, the polymer is converted into gaseous homologues of SiF_2, and these compounds are disproportionated on a silicon particle bed to deposit Si and regenerate SiF_4, which is recycled. The overall chemical reactions are:

(1) Formation of intermediate:

$SiF_4 + mgSi = 2SiF_2$ at 1350°C

(2) Polymer formation:

$xSiF_2 = (SiF_2)_x$ at -30°C

(3) Si production:

$(SiF_2)_x = Si + SiF_4 + Si_yF_z$ at 850°C.

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. Spark-source mass spectroscopy was used for composition analyses. A method of comparing the data for the product Si with data for semiconductor-grade Si was the basis for characterizing purity; the results were ambiguous. Resistivity measurements indicated the need for further removal of the electrically active impurities.

The chemical engineering, design, and costing for a 1 kg/h miniplant were accomplished in collaboration with Rafael Katzen Associates International, Inc. as consultants. A conceptual design was developed for a 100 MT/yr plant; the estimate capital cost was about $6,000,000. An economic analysis yielded a product cost of $7.71/kg.

This program was not continued through a demonstration phase using the miniplant. The decision to terminate was based on a technical evaluation.

7. Sodium Reduction of Silicon Tetrafluoride
(SRI International, Inc., JPL Contract No. 954471)

This program was intended to develop a process based on the reduction of SiF_4 by Na. The Si-containing raw material was hydrofluorosilicic acid (H_2SiF_6), a waste product of the fertilizer industry. In the process, H_2SiF_6 is converted into sodium fluorosilicate (Na_2SiF_6), which is in turn 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 Si in about three hours. Experimental results indicated that the precursor formation reactions proceeded with good yields; no problems in scaling up were predicted; the reduction reaction could be controlled by SiH_4 pressure, Na particle size, and reactant concentrations; and 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, such as Czochralski crystallization.

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 taken into account. Experimental results indicated that a modified Na delivery system would be needed, that the Si 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 Si product was recovered from the byproduct NaF by melt separation and also by a leaching method. Composition analyses led to the conclusion that a solar-grade Si would be obtained by a unidirectional solidification. Only the concentrations of B and Al would be near the critical values. The conclusions were that the use of carefully purified Na and modifications of the reaction process would lead to decreased contamination.

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

8. Carbothermic Reduction of Silicon Dioxide

(Texas Instruments, Inc., JPL Contract No. 954412)

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 Si was investigated. The proposed overall reaction was:

$$2C + SiO_2 \xrightarrow{2500^{o}C} Si + 2CO.$$

In a computer-aided thermodynamic analysis using iterative free energy minimization, the 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 Si as a condensate from a high-temperature plasma at various quench rates. The data indicated there was a maximum in the yield of Si, but the quench rate needed was beyond the experimental values and appeared to be too fast to be practical. In the reaction studies using a laboratory-scale experimental reactor, the maximum amount of Si 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 due to the poor heat transfer characteristics of the plasma flame. This and the low recoverable yields of Si were evidence of an unacceptable process and the contract was ended.

9. Rotary Chamber Reactor for Use in a Closed-Cycle Process (Texas Instruments Inc., JPL Contract No. 955006)

This program 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 $\approx$ \$7/kg (1980 \$, without profit). The program was terminated due to budget restrictions.

10. High-Capacity Arc Heater Process (Westinghouse Electric Corp., JPL Contract No. 954589)

This program was to develop a process 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. The demonstration of feasibility, an engineering analysis of the process, and the design of a test system to verify the reaction experimentally were completed as Phase I. 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. The results of the calculations led to the selection of Na. A similar set of calculations was used to determine the maximum concentrations of impurities possible in a molten-Si product at the operating conditions of the reactor.

The reduction reaction was characterized in small-scale laboratory apparatus under conditions approaching those planned for the process verification testing (a temperature of $3000^{\circ}K$). These conclusions were obtained: (1) a controlled reaction proceeds as predicted from the thermodynamic calculations; (2) Si can be separated and collected on a wall at a temperature above the dew point of NaCl; (3) the condensation rate is essentially predicted from the model calculations; and (4) larger collection rates should be obtained in a large-scale reactor due to the 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. Atomized Na injection using a sonic gas and a novel peripheral $SiCl_4$ injection feed were both shown to be suitable.

The testing facility was sized with a reactor capable of Si production at 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 $4000^{\circ}K$ was demonstrated.

A test run, which was aborted by shutdown set off by a flame-out condition of the waste burner, yielded Si material (97%) admixed with NaCl. The presence of the NaCl in the Si 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 Si 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 Si preparation and collection was not achieved; the capability of separating the products completely remains to be shown.

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

The program was terminated after the one run, due to budget restrictions and a Project program decision.

C. SUPPORTING PROGRAMS FOR PROCESS DEVELOPMENTS

1. Models and Computer Codes to Describe Silicon-Forming Reactions in Flow Reactors

(AeroChem Research Laboratories, Inc., JPL Contract No. 954862)

Two extremely useful models and computer codes were developed 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 the codes was demonstrated with an analysis of the system for the high-capacity arc-heater process for the Na reduction of $SiCl_4$, which was being developed under JPL contract by Westinghouse Electric Corp.

The first code developed was the CHEMPART code, an axisymmetric, marching code that treats the two-phase flow with models describing detailed gas-phase chemical kinetics, particle formation, and particle growth for complex systems. This code, based on the AeroChem LAPP (Low-Altitude Plume Program) 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. Also, depositions of heat, momentum, and mass (either particulate or vapor) on reactor walls are described. The second code is a modified version of the GENMIX boundary layer code, which 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 but has the virtue 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 in this program 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 Si(l) droplet formation. (The enthalpy is supplied by introducing large quantities of arc-heated H_2 in the case of the Westinghouse reactor.) On the other hand, large H_2 flows mean short transit times of gas through the reactor and, hence, short times for wall collection of Si. It is expected that an important 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.

2. Kinetics and Mechanisms of Silane Pyrolysis (AeroChem Research Laboratories, Inc., JPL Contract No. 955491)

The objective of this program was to characterize the kinetics and mechanism of the formation growth of Si particles from the decomposition of silane (SiH_4) at high temperatures. The need for this study became apparent early in the development of a reactor for the conversion of SiH_4 to Si (in the silane process at UCC) when it was recognized that considerable amounts of unusable fine particles of Si, formed in gaseous-phase nucleation reactions, are produced under some conditions of the thermal decomposition reaction. The experiments were aimed at determining the rates at which gaseous-phase species form Si-particle precursors, the time required to produce particles, and the rate of growth of Si seed particles injected into decomposing SiH_4 environment.

A high-temperature fast-flow reactor (HTFFR) was modified to study the decomposition of SiH_4 and the subsequent growth of particles. Particle growth measurements were made as functions of temperature (873^o to 1473^oK), 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^o from helium-neon (He-Ne) or argon $(A)^+$ lasers, were used to determine the apparent growth rates and absolute sizes of the particles. The extent of SiH_4 decomposition pressure was measured by infrared absorption spectroscopy. These measurements were used to determine 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 Si particles was studied in an environment of the complex reactions for the pyrolysis of SiH_4; the temperatures were 873^o, 1173^o, and 1473^oK. The seeded particles were either a commercial 5-μm Si powder or samples of the submicrometer powder product of the UCC free-space reactor. Attempts to observe Si atoms and the molecular species SiH, SiH_2, and $Si2H_6$ were unsuccessful.

It was found that:

(1) An initial growth of the particles occurs in an induction period of about 1 to 2 ms at 1200^oK, producing particles of less then 0.05 μm radius.

(2) The bulk of the particle growth occurs in 1 to 20 ms after the induction period, the particles growing to about 1 μm or larger at 1200^oK.

(3) The calibration of the Mie oscillations by Mie theory calculations agrees well with the determination of particle size by scanning electron microscope (SEM).

(4) The particles have a highly monodisperse size distribution.

(5) Particle concentrations decrease with increasing residence time.

(6) Perhaps two kinetic processes are occurring at the higher range of temperatures (>1173°K). It was suggested that:

  (a) There may be an optimum SiH_4 concentration above which further increases do not increase the growth rate proportionally.

  (b) Increasing the SiH_4 concentration increases the particle concentration to a limiting value.

  (c) Seeded particles grow faster with increasing temperature.

Finally, a model was developed to explain the growth of Si in a decomposing SiH_4 environment.

3. Fine Particle Growth in Silane Free-Space Reactor (California Institute of Technology, Work Order No. 61515)

The free-space reactor was the first apparatus investigated by UCC for the thermal decomposition of SiH_4 to Si. The studies were extended theoretically and experimentally at JPL by H. Levin, using the constant-flow pyrolyzer and silane-to-molten silicon reactors. The primary problem throughout these efforts was the fine particle product of mean mass diameter of tenths of μm, which was difficult to handle, transport, or melt; contamination due to the large surface also was a major concern.

The research at Caltech by Professor R.C. Flagan was started in 1980 with the program objectives to (1) describe the theory of the formation and growth of particles in the SiH_4 system and (2) develop a reactor and the reaction conditions for growing particles large enough to serve either as the seed for a SiH_4 FBR or as a material suitable for direct melting. In the first phase, the theory of nucleation quenching by aerosol particles was extended, and the conditions for growing larger particles was described. The design of a small, two-stage aerosol reactor was based on the theoretical analysis, having a first stage to generate particles by homogeneous nucleation and a second stage in which the conditions of SiH_4 concentration, temperature and gas velocity were controlled to accentuate particle growth while inhibiting the formation of new particles. Particles smaller than 0.5 μm were grown to particles having a mean mass diameter of 6.2 μm with 1% SiH_4 and to 9.2 μm with 2% SiH_4. The few particles >38 μm in diameter were found by electron microscope examination to have a fine structure, suggesting that this growth is by a combination of chemical vapor deposition and the scavenging of small clusters.

In the current research phase, the objectives are to formulate a more detailed theoretical treatment of the two final stages of nucleation quenching; begin the experimental determination of the correspondence between the chemical reaction kinetics and the particle growth mechanism; obtain data for reactor optimization analysis, and begin the examination of the means for particle separation, a procedure that could be adaptable to a direct melting process. Experiments will be performed in a larger, three-zone apparatus. Since this research is directed toward dealing with the fundamental questions of chemical reactions and particle growth mechanisms and toward designing an apparatus to obtain useable, large particles, it is of considerable value for the understanding of the phenomena in many reaction systems and reactors in which similar events occur.

4. Chemical Engineering and Economic Analyses
(Lamar University, JPL Contract No. 954343, and
Texas Research and Engineering Institute, JPL Contract No. 956045)

Contracts for independent chemical engineering analyses and economic estimates were instituted at the start of the Task process-development program to provide the necessary additional information for evaluations and comparisons of the development efforts. As part of the chemical engineering analyses, studies of the chemical, physical, and transport properties of the reactants and of the characteristics of the process systems were performed. Extensive descriptive data were obtained for 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. These data, secured from a critical use of the literature as well as from experimental measurements, were for the chemicals SiH_4, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiF_4, and Si; the data were presented as functions of temperature to facilitate use in research, development, and production engineering.

The chemical engineering analyses included activities for the formulation of the baseline conditions, reaction chemistry, process flowsheet, material balance, energy balance, property data, equipment design, major equipment list, and production labor requirements. The detailed data for raw materials, utilities, major process equipment, and labor were given in the process design packages, which in turn formed the bases for the economic analyses. The 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. The market prices were calculated taking into account a profit measured in terms of discounted cash flow or of return on investment.

Economic analyses involving preliminary process designs for 1000-MT/yr production plants were completed for the following processes: the Battelle Columbus Laboratories process for the Zn reduction of $SiCl_4$ in a fluidized-bed reactor; the conventional polycrystalline Si process using Siemens technology for deposition from $SiHCl_3$; the UCC process for the generation of SiH_4 and conversion to Si; and the Hemlock Semiconductor Corp. process for the generation of SiH_2Cl_2 and the deposition of Si in a modified Siemens reactor. The cost and profitability estimates from these analyses are:

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

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

5. Hydrochlorination of Metallurgical-Grade Silicon (Massachusetts Institute of Technology, JPL Contract No. 955382)

The importance of the hydrochlorination reactor in the UCC silane process and Hemlock dichlorosilane CVD process made additional investigations necessary for the full characterization of the reactor and its operating 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; and (4) the behavior of candidate materials of construction in the corrosive atmosphere of the reactor.

The results and conclusions were:

(1) The conversion of starting material to useful product is essentially 100%. The reaction rate increases rapidly and a higher conversion occurs with rising temperature. Although the rate of approaching equilibrium decreases with pressure, the conversion percentage increases. A higher $SiHCl_3$ yield takes place with increasing $H_2/SiHCl_3$ ratios, but the reaction rate is reduced.

(2) The reaction rate is independent of Si particle size in the range of $>37\ \mu m$ to $< 595\ \mu m$; 2 wt% Cu catalyst increases the rate twofold compared with 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 the silicide films that formed served to protect the reactor wall. Thus, previously observed corrosion problems appear to be due to 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 and that this reactor 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.

6. Radiantly Heated Fluidized-Bed Reactor (Oregon State University, JPL Contract No. 956133)

The objective of this research, under Professor O. Levenspiel, was to examine radiant heating of the particles of a fluidized bed as the first step in the consideration of alternative heating methods for the silane FBR system. The proposed advantages included the avoidance of heating through the reactor walls and thus the prevention of deposits of Si 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. One was the 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. The reactor design depends on this factor.

All of the experiments were performed in a nonreacting system without SiH_4. The 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 distribution are independent of the lamp power.

(2) The bed absorptivity is only affected by bed height insofar as it changes the distance from the source, is increased sharply with gas velocity, and is dependent on the reactor geometry so that designs that favor violent bed-bubbling with more particles ejected into the freeboard yield higher values.

(3) The heat transfer coefficient is dependent on the reactor geometry so that 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°C temperature at the distributor. It was shown that the distributor temperature could not be maintained using either a square or a round configuration. The 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 was 0.4 kWh/kg Si for the silane system using a multiorifice configuration.

Demonstrating the feasibility of heating a fluidized-bed reactor in this manner would require an extension of this study so that other factors could be investigated. The 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 fluidized-bed reactors is planned.

7. Hydrochlorination of Metallurgical-Grade Silicon (Solarelectronics, Inc., JPL Contract No. 956061)

This program was a continuation of the investigations performed under the JPL contract with the Massachusetts Institute of Technology, calling for extended studies of the thermodynamic properties and of the reaction kinetics of the hydrochlorination reaction with larger ranges of the pressure and temperature as the main variables. The study of corrosion phenomena under the reaction conditions for hydrochlorination was continued.

The studies of reaction kinetics showed that although the conversion yield of $SiHCl_3$ increases with pressure, the conversion rates decrease; that the rate and the yield increase with temperature under isobaric conditions; and that the rate and yield increase with the $H_2/SiCl_4$ ratio. The overall reaction was also shown to follow a pseudo-first-order kinetics model. The variation of the first-order rate constant with temperature was used to calculate a value for the activation energy of 13.2 kcal/mol.

An investigation of deuterium isotope kinetics effects revealed no isotope effects, indicating that H_2 is not directly involved in the rate-determining step of the reaction. A model of the reaction mechanism based on this result was proposed.

The corrosion tests were carried out for 87 hours under reactor conditions of 300°C, 300 lb/in.^{2} gauge, and $H_2/SiCl_4$ feed ratio of 2.0. The system contained ≈0.5% HCl and a mixture of chlorosilanes. The materials tested were carbon steel, Ni, Cu, Monel, 304 stainless steel, Incolloy 800H, and Hastelloy B-2. All of the samples gained weight due to silicide film formation. Analysis by SEM showed diffusion of Si into the base metal. The results showed that the film depositions were greater for the metals than for their alloys and that alloys with the higher melting elements permitted the least amounts of film formation. The conclusions were that stainless steel, Incoloy 800H, and Hastelloy B-2 are suitable materials of construction for the hydrochlorination reactor.

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

D. EFFECTS OF IMPURITIES ON SILICON PROPERTIES AND SOLAR-CELL PERFORMANCE

1. Effects of Impurities and Processing on Silicon Solar Cells (Westinghouse R&D Center, JPL Contract No. 954331)

Information regarding the effects of impurities on photovoltaic cell performance permits the linking of the cell description with polycrystalline Si composition. In turn, this relationship enables chemical engineering and production plant design analyses of the requirements for process purification units. This program was established to study the effects of impurities, processing procedures, and contaminant interactions on the properties of Si and the performance of terrestrial solar cells. During the program, Czochralski, float-zone, and polycrystalline ingots, prepared by Dow Corning Corp., and dendritic web ribbons, were grown with controlled additions of impurities, using boron and phosphorus as the electrical dopants. The impurity elements included those present in mgSi, which is used as the raw material for many refining processes, and those that might be added adventitiously from subsequent processing to produce single-crystal ingots, wafers, and solar cells. The elements were gold (Au), silver (Ag), aluminum, carbon (C), calcium (Ca), chromium (Cr), cobalt (Co), copper, iron, magnesium, manganese (Mn), niobium (Nb), nickel (Ni), palladium (Pd), tin (Sn), tantalum, titanium (Ti), vanadium (V), tungsten (W), zinc, and zirconium (Zr). The impurity concentrations ranged from 10^{11} to 10^{18} atoms/cm^3.

In Phase I a functional analytical model was formulated. 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, short-circuit current, and cell efficiency were related to the concentrations of the impurities. Data obtained from 52 Czochralski ingots and 44 dendritic-web specimens, which were deliberately doped with particular impurities, were shown to conform closely to the model. The 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/cm^3 of Ti or V while more than 10^{15} atoms/cm^3 of Cu were needed for the same effect. The behavior of multiply doped materials and cells were successfully predicted using the model and experimentally measured relationships of lifetime and efficiency values.

Tolerable impurity concentrations for a polycrystalline material feedstock for Czochralski processing were estimated using crystal-growth impurity-partitioning behavior and the relationships derived in this study for the effects of specific impurity concentrations on solar cell properties. The degree of impurity toleration in the feedstock is primarily species-dependent, as a consequence of the specific effects on cell performance. The limiting condition for acceptable purity for a certain crystal growth rate depends on the selected solar-cell performance level and not on crystal breakdown. Continuous, rather than sequential, feeding is advantageous when using a melt-replenishment method, due to 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.

In Phase II the effects of thermal treatments, crystal growth rate, base doping concentration and type, grain-boundary structure, and carbon-oxygen metal interactions were studied. That the impurity-induced cell performance loss is primarily due to the reduction in base diffusion length was firmly established, using data from more than 4000 cells. 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 due to junction excess currents induced by precipitates. Considerably less cell-performance reduction occurred in n-base cells than in p-base cells for the impurities Ti, V, Cr, and Mn. The data to demonstrate that this is a general conclusion were not obtained. The experimental result showing 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 led to the hypothesis that in the low-resistivity material, band-gap narrowing combined with the creation of excess numbers of traps (compared with the high resistivity material) compromise the beneficial effects of the larger open circuit voltage.

In the 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.

Tradeoff analyses using the 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., Czochralski and 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 the studies of the effects of thermochemical gettering treatments, base dopant concentration and type, and grain-boundary--impurity interactions were continued along with investigations of the effects of nonuniformity 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 ±10%. From data obtained from aging experiments at high temperatures, it was shown that additional decreases in cell performance are functions of diffusion rates; the projected stabilities for Mo and Ti were beyond 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. The electrical activity of impurities decreased due to precipitation in the vicinity of the grain boundaries, and this reduction was directly related to the specific impurity diffusion coefficient.

The extensive data base and the model equations derived in these studies can be used for the assessment of the utility of a silicon material with a particular 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 photovoltaic cells indicated that the sensitivity of the cell performance to impurities would increase and that 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 ($\approx 100\ \mu m$) base widths.

These studies have provided experimental data and analytical models to explain the effects of impurities on the properties of Si materials and the performance of photovoltaic 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 instances the scope of the studies should be extended. In particular, the area of high-efficiency cells should be investigated fully to characterize impurity effects for advanced-stage cells.

2. Effects of Impurities
(Monsanto Research Corp., JPL Contract No. 954338)

This program 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 Czochralski (Cz) and float-zone (Fz) procedures. Energy conversion efficiencies were measured against a standard solar cell. Most of the 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 Si material. For example, the values were (in 10^{15} atoms/cm^3): 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; the direct relationship of 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 Si) 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. A close correlation of base material minority carrier lifetime and cell efficiency was shown. Diffusion and other processing steps caused parallel changes in these values for materials containing impurities; this result indicated 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 O at a concentration of about 10^{18} atoms/cm^3 in Cz Si and $<10^{16}$ atoms/cm^3 in Fz Si 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 Si materials, of oxygen on impurities in Si, of impurities on n-base materials, and of the presence of more than one impurity.

3. Lifetime and Diffusion-Length Measurements
(Northrup Research and Technology Center, JPL Contract No. 954614)

Obtaining accurate, sensitive, and reproducible data for minority carrier recombination lifetime and diffusion length was shown to be essential in the investigations of impurity effects on cell performance by Westinghouse et al. The intent of this study was to assess the applicability of particular 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 techniques. Minority carrier lifetime was measured using the method of transient photoconductivity decay (PCD) and steady-state photoconductivity (SSPC). Diffusion lengths were determined on solar cells and other test structures by means of short-circuit measurements using either point-source excitation from a scanning electron microscope or uniform generation derived from a Co^{60} gamma source or band-edge light.

Excellent agreement between a bulk measurement and a device measurement of diffusion length was found, and there was moderate agreement of the diffusion-length equivalent lifetime with the lifetime measured by photoconductivity decay. Earlier conclusions concerning the errors induced in bulk lifetime measurements by trapping effects, despite the use of background light to fill the traps, were confirmed in the course of establishing the generation rate in the SSPC method. 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 in order to fill traps in SSPC measurements.

The bulk lifetime data obtained by steady-state photoconductivity measurements of 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 particularly 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 appeared to be considerably less sensitive to the presence of Al, Ni, and Cu. In the case of Ni, and possibly Al, this may have been due to the low fraction of the total concentration that is electrically active.

The lifetime data derived from diffusion-length measurements on devices indicated that the 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. The data for devices indicated somewhat greater sensitivity to the presence of Cr, Ti and Ni than was observed in the bulk samples, although the sensitivity to Fe in the device data was considerably reduced. A 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 program were: (1) The consistency of values among the very different experimental methods for measuring lifetime and diffusion length was verified. (2) The SSPC method was established for measurements to about 10 ns and under adverse conditions with respect to minority carrier trapping and surface recombination. (3) The extreme sensitivities of life-time values to the presence of specific impurities and the concentration dependencies found by others were verified.

4. Studies of the Effects of Impurities
(C.T. Sah, Inc., JPL Contract No. 954685)

This program of theoretical and experimental studies was directed toward determining the effects of impurities on the properties of Si and on the characteristics of solar-cell performance, taking 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 procedures 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 the computation of the exact steady-state characteristics. The effects of 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 open-circuit voltage were studied. A new technique 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 was suggested.

Then solutions were obtained using the model 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 of Ti and Zn as impurities in high-efficiency back-surface-field (BSF) cells were considered.

The complex dependences of the peak conversion efficiency of a back-surface-field solar cell on thickness and on the concentrations of recombination and dopant impurities was investigated. 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 a 3:1 range of cell thickness from 30 m to 100 m, was found for the efficiency-thickness function. An optical reflecting back surface was shown to give only a slight improvement in this thickness range.

The effects of electrical short circuits across the BSF junction at the perimeter of a cell was analyzed by applying the low-level, one-dimensional analytical theory to a developed cell geometrical device model. It was shown that for small-area, thin, large-base-diffusion-length cells the reduction in open-circuit voltage and efficency 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 open-circuit voltage of a BSF solar cell. A developed perimeter device model was used. It was shown that (1) the decrease in V_{OC} is nearly independent of the defect area when its dimension is less than about 30% of the minority carrier diffusion length in the base; (2) the decrease in V_{OC} is mainly due to 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) the reduction in the V_{OC} as a consequence of defects across the BSF junction increases as the cell is made thinner; and (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 open-circuit voltage 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 anaytical 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 the 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.

5. Cell Measurements of Impurity Effects (Solarex Corp., JPL Contract No. 955307)

The purpose of this program was to obtain data on the effects of impurities on performance of solar cells fabricated and measured by a commercial cell manufacturer. These separately determined data and conclusions were compared with the information secured by Westinghouse and Monsanto to ensure the validity of the overall conclusions of the Task program on the effects of impurities. The cells were fabricated and analyzed using aerospace technology and quality-assurance procedures to ensure that measured variations of cell performance were due to impurity effects. The wafers were prepared from deliberately doped Czochralski single-crystal ingots. Cells fabricated from uncontaminated semiconductor-grade Si 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 AMO efficiencies of nearly 13% at 25°C. No cross-contamination of control or monitor cells was observed. The performance degradation in the test cells was principally due to 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/cm^3, was caused by the presence of Ti, V, and Ta. Cell performance appeared 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.

6. Cell Measurements of Impurity Effects (Spectrolab, Inc., JPL Contract No. 954694)

The purpose of this program was to obtain data on the effects of impurities on performance of solar cells fabricated and measured by a commercial cell manufacturer. These separately determined data and conclusions were compared with the information secured by Westinghouse and Monsanto to ensure the validity of the overall conclusions of the Task program on the effects of impurities. Using conventional aerospace process technology for solar-cell fabrication, 63 lots of wafers from single-crystal ingots deliberately doped with impurities were studied. The Si sources were Dow Corning-Westinghouse crucible-grown Si, Monsanto crucible-grown Si, and Monsanto float-zone silicon. In the measurement procedure, quality control was monitored, and cross-contamination was prevented. The cell performance was determined by electrical and spectral measurements. Except in one case, the properties of cells within each impurity concentration group were extremely consistent electrically and spectrally. There was good correlation between the electrical outputs and the spectral response data. The elements that caused decreases in efficiency were Al, Cr, Fe, Ni, Ti, V and Zr. For the last three, concentration levels below 10^{13} atoms/cm^3 appreciably affected efficiency. In many cases performance losses could only be related to impurity limits, since more exact concentration data were not available. 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 results generally verified the measurements performed by Westinghouse on the same materials.

7. Composition Measurements by Analytical Photon Catalysis (Aerospace Corp., JPL Contract No. 955201)

The objective of this research was to assess the applicability of the photon catalysis technique for composition analyses of Si samples. The technique was evaluated as a detector and as a concentration measurement technique for the impurities Al, Cr, Fe, Mn, Ti, V, Mo, and Zr. 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 Si matrices was studied. The evaporation process was shown to be congruent; thus, the spectral analysis of the vapor will yield 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 Si. 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 a laser microprobe and photon catalysis technology.

E. JPL IN-HOUSE RESEARCH

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

1. Silane Deposition Reactor Investigations (JPL Chemical Engineering Laboratory)

Limiting the JPL chemical engineering effort to studies of chemical reactors suitable for the decomposition of SiH_4 to Si was a consequence of an early conclusion of the Silicon Material Task that the SiH_4 process had a high probability of achieving the Task goal and that the development of a deposition reactor for the SiH_4 process would be a formidable problem. Three types of reactors were studied: the FBR, the FSR, and the SiH_4-to-molten-Si reactor (SMSR). The most intensive effort was for 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 that contract. At JPL the research on this type of reactor was carried out using the name Continuous-Flow Pyrolyzer (CFP). In conjunction with the experimental studies, a theoretical analysis was formulated to provide a quantitative description of the kinetics of the heterogeneous pyrolysis of SiH_4 at relatively low temperatures. The proposed mechanism involved a sequence of homogeneous gas-phase pyrolysis, the coagulation of particle clusters, and the decomposition of SiH_4 on the clusters. The large surface area necessary for the heterogeneous pyrolysis is provided under conditions in which rapid generation of very small particle clusters occurs. The kinetics of SiH_4 decomposition are rapid enough even at low temperatures to give practical production rates. The analytical treatment yielded a general equation for heterogeneous pyrolysis and a specific equation for the conditions of a free-space reaction.

The influences of temperature (800° to 850°C) and Si seed particles on the formation and growth of Si particles from SiH_4 pyrolysis were determined in a brief experimental study. The conditions of gas flow, pressure, and the SiH_4 concentration (4%) were kept constant. It was found that no chemical vapor deposition took place on unheated seed particles introduced into the system. The main product was a fine power (about 0.1 μm dia) formed by homogeneous gas phase nucleation. Some dense, thin deposits also formed on the hot surfaces by chemical vapor deposition.

The experimental results were described using a general concept in which successive reaction steps occur. The preparation of 0.3-μm-sized particles was found to be the overall product of this work. The values of reaction-velocity constants and surface-reaction efficiency that were experimentally obtained appeared to support the mathematical model. A correspondence was shown between the model and the experimental results; other models of the overall mechanism may be as valid. This work was terminated in favor of emphasis on the development of the FBR for the silane process.

The first step of the FBR development program was to perform a series of theoretical studies to model the reactor in the SiH_4 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. Special attention was given to the phenomena involved in particle growth. A computer program was derived from the simple description of the first study. It was intended that critiques of the assumptions and treatment of this model would lead to a more sophisticated model.

In the following study, integrated mathematical models were developed to describe Si particle growth. The assumption was that the particle growth was the direct result of heterogeneous deposition, the depositing particles being the result of a sequence of forming Si nuclei and then of clustering the nuclei into very small particles. A diffusional growth mechanism was used as the basis for the model. This model emphasized the need for rigorous experimental information regarding the mechanisms and kinetics of Si particle growth. The conclusions from these studies provided an impetus for the use of expanded sets of the operating conditions for an experimental reactor. Later, the models, coupled with the experimental results, 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. The objective was to determine whether reasonable concentrations of SiH_4 could be used without the generation of large amounts of fine particles, an undesirable condition for FBR operation. The limiting SiH_4 concentration of 1% under epitaxial deposition conditions, which had been cited in a previous study, was surpassed in these experiments in which concentrations up to 15% SiH_4 in H_2 were used; the temperature range was 550° to 700°C, and the 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% SiH_4 concentrations. A concentration of 10% was a milestone, since an economic analysis had indicated that it was the value suitable for reaching the Task economic goal using the SiH_4 process.

In the next phase, an extensive experimental program was conducted with a 2-in.-ID FBR. The experimental variable ranges were greatly extended: the temperature limit was pushed to 800°C, and the concentrations were 20%, 40%, 60%, 76%, and 100%. In general, the amount of fine particles increased with temperature, with a twofold change over the range of 650° to 800°C using 20% SiH_4, and increased with SiH_4 concentration, being 10% at 100% SiH_4. The startling results were that very small amounts of fine particles were formed at high SiH_4 concentrations. This finding, so different from those obtained in the epitaxial deposition experiments, was explained using a concept of the scavenging of the submicrometer Si clusters by the fluidized-bed particles.

The problem of particle agglomeration was also studied, since agglomeration is a catastrophic condition in which a high density of particles forms and causes a bridge of particles that very quickly stops fluidization. A properly operating bed was maintained by adjusting the gas velocity, making sufficient increases to override the effects of higher silane concentrations.

A 6-in.-ID FBR is being used in the third phase of this research. The first objectives were: (1) to design a cooled distributor plate and to determine the operating conditions necessary to obtain a plate temperature of <400°C concurrently with a bed temperature of 650°C (to prevent SiH_4 decomposition in the distributor); (2) to determine the feed-concentration limit and the operating conditions for dense, coherent particle growth and minimum fine particle formation; and (3) to obtain kinetic data to be used for the formulation of a model for the deposition mechanism and the operating of the FBR. After a series of modifications of the plate cooling and of the heater geometry, the reactor was operated under the desired temperature conditions. The capability of running with high SiH_4 feed concentrations was demonstrated in a group of runs. In these, a deposition rate of 1 kg/h was achieved for a 90-minute run at 20% SiH_4; step-wise changes in SiH_4 concentration ranging from 20% to 100% over a two-hour period gave an overall deposition rate of 3 kg/h; and in a 3-h run at 80% SiH_4 the rate was 3.5 kg/h. The collected dust was less than 11% in all cases, and there was no wall deposit or bed agglomeration. Thus, the feasibility of operation in high SiH_4 concentration ranges has been shown. Research to define the deposition mechanism and to characterize the SiH_4-FBR system fully continues.

2. Silicon Materials Research
(JPL Silicon Materials Research Laboratory)

The Silicon Materials Research Laboratory was involved in experimental research in the areas of the effects of impurities on Si material properties, methods of measuring concentrations of elements in Si in the ppba range, and the techniques for consolidation of the submicrometer Si powder obtained from the operation of the UCC free-space reactor. The research on impurity effects was done in collaboration with the research 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 the efforts of the in-house program. In the consolidation work several apparatuses for melting the fine powder were tried with varying degrees of success.

The emphasis was on the determinations of the energy levels and electrical activities associated with specific impurities in support of the Task program dealing with impurity effects. The thermally stimulated capacitance method (TSCAP) 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 capability of detecting some elements that are not measurable by other techniques. To secure the data, great care was taken to ensure accurate capacitance and temperature measurements; to prepare the diodes with particular attention paid to methods of preventing surface channel leakage and intersurface irregularity; and to be especially diligent in the resolution of overlapping signals originating from two closely adjacent trapping levels. Automated techniques for use with TSCAP and VSCAP were introduced. These techniques were used to detect electrically active impurity concentrations of as little as 10^{10} atoms/cm^3 in a substrate having 10^{14} atoms/cm^3 concentration of a primary impurity. These data, along with those obtained under the various contracts, formed an information base that was used to develop an understanding of the major physical mechanisms and chemical reactions involved in the effects of impurities.

Aside from analyzing the measurement techniques being developed and the composition data being gathered under the JPL contracts, the effort in the area of impurity concentration determinations was directed toward developing the procedures and capabilities of the Zeeman atomic absorption spectrometer. This instrument utilizes the Zeeman effect on a resonant transition to correct automatically for background interference. Trace elements can be measured directly without need of 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. A technique for sampling submicrometer powder was developed. The preliminary calibrations 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 elements.

Since the free-space reactor offered the great advantages of 100% yield for the conversion of SiH_4 to Si, very low energy use, and simple design, the problem of devising a method for the consolidation of the submicrometer powder product was also tackled. The effort was directed to the development of the technique of pedestal melting, in which the powder is introduced into a molten Si 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.