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LOW COST SOLAR ARRAY PROJECT

Experimental Process System Development Unit for Producing
Semiconductor-Grade Silicon Using the Silane-to-Silicon Process

Quarterly Progress Report, April-June 1979

Work Performed Under Contract No. NAS-7-100-954334

Union Carbide Corporation
New York, New York

MASTER

U.S. Department of Energy

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Solar Energy

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low cost solar array project

EXPERIMENTAL PROCESS SYSTEM DEVELOPMENT UNIT FOR
PRODUCING SEMICONDUCTOR-GRADE SILICON USING THE
SILANE-TO SILICON PROCESS

MASTER

QUARTERLY PROGRESS REPORT

April – June 1979

UNION CARBIDE
CORPORATION

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ABSTRACT

This report covers the work performed in April, May, and June 1979 on JPL/DOE Contract 954334, Phase III.

The Experimental Process System Development Unit (EPSDU) engineering effort was formally started in June and a preliminary project plan was issued defining project scope, schedule, cost, and engineering team responsibilities. The engineering work started with a process design package containing information based on the most recent stream catalog and process flow diagram. Activities recently initiated include EPSDU layout, equipment specifications and Requests for Quote (RFQ), preliminary Piping and Instrumentation (P&I), free-space reactor and distillation column designs, and an electrical one-line drawing.

The process design is incomplete in a few areas and the Supporting R & D effort has been directed to address the uncertainties. A small waste treatment apparatus is being assembled to provide essential information for control system design, materials of construction, and utility requirements. The apparatus should be in operation by late August. This scheme, if successful, will treat waste streams and produce by-products that have some commercial value.

Various improvements are being made to the free-space reactor PDU to enable operation for a long duration at design throughput without powder build-up in the reactor, and without exposing the silicon powder to the atmosphere. Equipment design and the P & I diagram have been completed. The apparatus for the fixed-bed deposition experiments has been designed and the equipment purchase orders have been issued. Experiments will be conducted to determine the critical silane concentration for homogeneous/heterogeneous decomposition and to establish the silicon deposition rate.

The melting/consolidation system will be developed by an outside firm(s) that, under a subcontract to Union Carbide, has extensive

experience and background in silicon melting and solidifying. The RFP is being prepared.

Although more tests are planned to quantify the findings, experiments with fluidized beds produced some promising trends:

- Silicon particles can be heated capacitively with minimal sintering.
- High-purity silicon appears to sinter much less than metallurgical-grade silicon.
- Silicon particles can be segregated by size in a boot located below the bed.

Work is in progress to develop quality control procedures for EPSDU. The two present programs, directed toward detecting trace impurities in silane, are:

- Reactive chromatographic technique for hydrocarbon detection - this appears feasible.
- Electrical measurements of electrically-active impurities - A reactor was designed to deposit silicon from silane onto a slim silicon seed rod.

These and other Q.C. apparatus will eventually be housed at the EPSDU site. The streams requiring analysis and the analytical methods are being identified for the EPSDU.

SECTION I. INTRODUCTION

This report covers the work performed in April, May, and June 1979 on JPL/DOE Contract 954334, Phase III.

The overall objective of the LSA Silicon Material Task is to establish a chemical process for producing silicon at a rate and price commensurate with the production goals of the LSA project for solar-cell modules. This material must be suitable for utilization in the large-area sheet process and in the automated process for the fabrication of solar cells having satisfactory physical and electrical performance characteristics.

As part of the overall Silicon Material Task, Union Carbide developed the silane-silicon process and advanced the technology to the point that it has a definite potential for providing high-purity polysilicon on a commercial scale at a cost of \$14/kg by 1986 (1980 dollars). This work, completed under Phases I and II of the contract, provided a firm base for the Phase III program (initiated in April 1979) aimed at establishing the practicality of the process by pursuing the following specific objectives:

- Design, fabricate, install, and operate an Experimental Process System Development Unit (EPSDU) sized for 100 MT/Yr to obtain extensive performance data to establish the data base for the design of commercial facilities.
- Perform supporting research and development to provide an information base usable for the EPSDU and for technological design and economic analysis for potential scale-up of the process.
- Perform iterative economic analyses of the estimated product cost for the production of semiconductor-grade silicon in a facility capable of producing 1000 MT/Yr.

This process for preparing semiconductor-grade silicon in the EPSDU from metallurgical-grade (M-G) silicon is based on a well-integrated arrangement of purification steps that provides a cost-effective process system.

The three basic steps entail converting M-G silicon to trichlorosilane, re-distributing the trichlorosilane to produce silane, and thermally decomposing the silane to form polycrystalline silicon powder. The powder is then melted and the molten silicon is cast into rods for subsequent fabrication of solar cells.

The technical progress presented in this report is arranged according to the Work Breakdown Structure (WBS) shown in Table I.

TABLE I WORK BREAKDOWN STRUCTURE

1.1 DESIGN & PROCUREMENT	1.4.4 INITIAL FEASIBILITY DEMO
1.1.1 PROCESS DESIGN	1.4.4.1 Preparation
1.1.1.1 Process Design Update	1.4.4.2 Steady-state 15-day Run
1.1.1.2 Support for Engineering Design	1.4.4.3 Sample Preparation & Delivery
1.1.1.3 Support for Equipment Design/Specs	1.4.5 DATA GENERATION & ANALYSIS
1.1.2 ENGINEERING DESIGN	1.4.5.1 Hydrogenation
1.1.2.1 Control Systems	1.4.5.2 Distillation/Redistribution
1.1.2.2 Layout	1.4.5.3 Pyrolysis/Consolidation
1.1.2.3 Electrical	1982 LSA Goals
1.1.2.4 Safety	1.4.5.4 Waste Treatment & Auxiliaries
1.1.3 EQUIPMENT SPECIFICATION/PROCUREMENT	1.4.6 SILICON CONSOLIDATION R & D, 1986 GOALS
1.1.3.1 Mechanical	1.4.6.1 Hydrogen-Atmosphere Operation
1.1.3.2 Electrical	1.4.6.2 Large-Diameter Rod Casting
1.1.3.3 Instruments & Controls	1.4.6.3 Sample Preparation & Deliveries
1.1.3.4 Other Instruments	1.4.7 OFF-SITE QC ANALYSIS
1.1.4 INSTALLATION DRAWINGS	1.4.7.1 Sample Preparation & Deliveries
1.1.4.1 Site	1.4.7.2 Analysis
1.1.4.2 Civil	1.4.8 FINAL PERFORMANCE RUN
1.1.4.3 Mechanical & Piping	1.4.8.1 Preparation
1.1.4.4 Electrical	1.4.8.2 Optimized Performance Run
1.1.4.5 Instrumentation	1.4.8.3 Sample Preparation/Delivery, Data Anal.
1.1.5 ENVIRONMENTAL	1.4.9 EQUIPMENT DURABILITY ASSESSMENT
1.1.5.1 Environmental Impact Study	1.4.9.1 Hydrogenation, Distillation, Redistribution
1.1.5.2 Noise	1.4.9.2 Silane Pyrolysis & Silicon Consolidation
1.1.5.3 Permits/Special Studies	1.4.9.3 Waste Treatment & Auxiliaries
1.1.6 COST ESTIMATE	1.4.10 SHUTDOWN
1.2 EPSDU-EQUIPMENT FABRICATION/DELIVERY	1.5 COMMERCIAL PROCESS ECONOMIC ANALYSIS
1.2.1 MECHANICAL	1.5.1 PROCESS DESIGN
1.2.1.1 Compressors	1.5.1.1 Functional Package
1.2.1.2 Pumps	1.5.1.2 Functional Package Update No. 1
1.2.1.3 Unclassified	1.5.1.3 Functional Package Update No. 2
1.2.2 ELECTRICAL	1.5.2 ENGINEERING DESIGN
1.2.2.1 Motor-Control Center	1.5.2.1 Engineering Package
1.2.2.2 Power Wiring	1.5.2.2 Engineering Package Update No. 1
1.2.2.3 Unclassified	1.5.2.3 Engineering Package Update No. 2
1.2.3 INSTRUMENTS & CONTROLS	1.5.3 COST ESTIMATING
1.2.3.1 Field Instruments & Controls	1.5.3.1 Baseline Estimates
1.2.3.2 Panel Instruments	1.5.3.2 Cost Estimate Update No. 1
1.2.3.3 Data Collection System	1.5.3.3 Cost Estimate Update No. 2
1.2.3.4 Unclassified	1.5.4 ASSESSMENT & REPORTING
1.2.4 OTHER EQUIPMENT	1.5.4.1 Baseline Assessment
1.2.4.1 Tanks/Bins	1.5.4.2 Assessment Update No. 1
1.2.4.2 Heat Exchangers	1.5.4.3 Assessment Update No. 2
1.2.4.3 Reactors	1.6 PROCESS SUPPORT R & D
1.2.4.4 Columns	1.6.1 FREE-SPACE REACTOR DEVELOPMENT
1.2.4.5 Filters	1.6.1.1 PDU Experiments
1.2.4.6 Solids Handling	1.6.1.2 Theoretical Analysis
1.2.4.7 Unclassified	1.6.2 MELTING/CONSOLIDATION
1.3 EPSDU-INSTALLATION & CHECKOUT	1.6.2.1 Melter System Design
1.3.1 SITE EVALUATION	1.6.2.2 Hydrogen-Atmosphere Tests
1.3.2 INSTALLATION	1.6.2.3 Large-Diameter Rod Casting
1.3.2.1 Site	1.6.2.4 Shotting Feasibility Assessment
1.3.2.2 Civil	1.6.3 FLUID BED DEVELOPMENT
1.3.2.3 Structural	1.6.3.1 Fixed-Bed Deposition
1.3.2.4 Mechanical	1.6.3.2 Fluidization-Experiments with Inert Gas
1.3.2.5 Electrical	1.6.3.3 Evaluation-Fixed Bed/Fluidization
1.3.2.6 Instruments & Controls	1.6.3.4 Fluid-Bed Pyrolysis
1.3.2.7 Other Equipment	1.6.3.5 Fluid-Bed Process Design for EPSDU
1.3.2.8 Piping	1.6.3.6 Fluid-Bed Model Update
1.3.3 CHECKOUT	1.6.4 QUALITY CONTROL
1.3.3.1 Safety	1.6.4.1 Silane Analysis - Slim-Rod Deposition
1.3.3.2 Operational	1.6.4.2 Silane Analysis - Direct Measurement
1.4 OPERATION	1.6.4.3 Silane Analysis - Epitaxy
1.4.1 PREPARATION	1.6.4.4 Float-Zone Refining
1.4.1.1 Operating Manual	1.7 MANAGEMENT AND DELIVERABLES
1.4.1.2 Training	1.7.1 PROJECT MANAGEMENT
1.4.1.3 Inspection & Calibration	1.7.1.1 Administration
1.4.2 START-UP	1.7.1.2 Contract Maintenance
1.4.2.1 Waste Treatment	1.7.2 PROGRAM MANAGEMENT
1.4.2.2 Hydrogenation	1.7.2.1 Technical Direction
1.4.2.3 Distillation/Redistribution	1.7.2.2 Cost/Schedule/Documentation Services
1.4.2.4 Pyrolysis/Consolidation	1.7.3 DELIVERABLES
1.4.3 MODIFICATION	1.7.3.1 EPSDU Facility
1.4.3.1 Design	1.7.3.2 Material Samples
1.4.3.2 Procurement	1.7.3.3 Data
1.4.3.3 Installation	

SECTION II. TECHNICAL ACTIVITIES (BY WBS NUMBER)

1.1 EPSDU - DESIGN/PROCUREMENT

During Phases I and II of the program which ended in March 1979, Union Carbide's Silane-to-Silicon process design was essentially completed. Based on this, the EPSDU engineering effort was initiated under Phase III on 1 June, 1979. During the next five months, a comprehensive engineering design which will include environmental and safety considerations will be completed in sufficient detail to obtain vendor quotations. The areas covered by the engineering design will include the process equipment, electrical equipment, control systems, and facility layout. In addition, a quality cost estimate will be completed for assembling the EPSDU.

1.1.1 Process Design

A process design package was issued on June 1, 1979 (Ref. 1) to start the engineering effort. It contains a mass balance, stream catalog, equipment specifications, safety information, and other background information in select areas. Since layout is a key area needing much development, all equipment has been rough-sized (physical dimensions and sketches showing configuration) to support this work. An analysis was made of the data collection points and sample taps required for definition of the data collection system and quality control lab.

In support of engineering design, process waste burner experiments will be conducted. These tests will address uncertainties in the control system design, materials of construction, and utility requirements to establish the waste treatment system rangeability. Currently, the controls must be based on a pure feed-forward control system, which anticipates disposable wastes by measuring individual waste flows and also calculates requirements of natural gas and combustion air. By accurately measuring the flame temperature, the feed-forward controls can be simplified to a single flow measurement with the flame temperature feeding back a fine tuning adjustment. An optical pyrometer will be calibrated for this low emissivity flame. Materials of construction

uncertainties will be checked by a metallurgical examination after operation. Rangeability testing will determine the degree to which the burners can handle surges (such as pressure reliefs) without loss of stable flame.

1.1.2 - 1.1.6 Engineering Design, Equipment Specification/
Procurement, Environmental, and Cost Estimating

Engineering activities initiated include plant layout, equipment specifications and RFQs, preliminary P&I, free-space reactor and distillation column design, and electrical one-line drawing.

1.6 PROCESS SUPPORT R&D

1.6.1 Free-Space Reactor Development

1.6.1.1 Process Development Unit (PDU) Experiments

The free-space reactor PDU was transferred from Parma to Tonawanda in preparation for a long-term, steady-state operation at the design throughput. After modifications, the PDU will be reassembled in an explosion-proof test facility.

The P & I diagram, presented as Figure 1, identifies all required instrumentation for control and operation of the free-space reactor. Various improvements being made to the PDU include:

- Free-Space Reactor Shell - The shell, shipped from Parma, is made of monel and is substantially de-alloyed, especially in a 1-foot section of the hot zone. Flakes of zinc had accumulated on the outside of the reactor cylinder and the wall was less than half of the original thickness. A shell made of Incoloy 800 was ordered, since this alloy is metallurgically much better suited for this application than monel.

- Silicon Hopper - A large hopper was designed to hold a 2½-day inventory of silicon powder. The fabrication drawings were completed and the materials have been ordered.

- Reactor Head Flange - The top head assembly for the pyrolysis reactor was re-designed to incorporate a remote controlled actuator for a mechanical scraper. Construction drawings reflecting this change are currently being prepared. A small feeder cone is also being designed for the bottom of the silicon product hopper to facilitate withdrawing powder by adding fluidization gas.
- Induction Power Supply - New capacitors were installed in the induction heating power supply to replace the previous PCB-filled units that are environmentally unacceptable. New power leads are being acquired for the power supply.

1.6.1.2 Theoretical Analysis

Free-space pyrolysis is being modelled analytically to provide a better understanding of the flow and temperature characteristics inside a free-space reactor of any given configuration. The objective is to characterize a pyrolysis system in which silane is pyrolyzed away from the reactor walls but the powder is retained in the pyrolysis zone long enough to grow in size for easier handling.

Dr. F. M. Galloway of Cleveland State University visited us on June 20, 1979, and presented his analytical model work on the free-space reactor. Plans for future modelling in this area are being formulated. The possibility of using a generalized computer model from combustion-related literature will be explored.

1.6.2 Melting/Consolidation

A method must be developed to melt and consolidate the free-space reactor powder without exposing it to the atmosphere to preclude possible contamination. One or two commercial silicon melter vendors will be selected to develop a system for transporting silicon powder to the melter and to create a consolidation scheme that is reliable, cost effective, and keeps the addition of impurities to an absolute minimum.

A statement of work and terms and conditions are being written for the subcontract which will have two distinct objectives. The first consists of an R & D effort required to experimentally demonstrate the operability of a melter system design and to prepare a functional design package for the EPSDU melter system. The second consists of detailed engineering design, fabrication, and delivery of the EPSDU melter system.

1.6.3 Fluid Bed Development

1.6.3.1 Fixed Bed Deposition

Two types of experiments using a small fixed bed are planned. One is to determine the critical concentration of silane at a given bed temperature below which favorable heterogeneous decomposition of silane takes place. The other is to determine the rate of silicon deposition on seed particles at a given bed temperature and feed-silane concentration. These tests will be conducted in the temperature range of 600 to 900° C. Data obtained from these experiments, along with those from the inert gas fluidization and heating tests, are required for the evaluation and design of the fluid-bed pyrolysis PDU.

The experimental program being developed will be conducted in a 1-inch diameter quartz tube. The first series of experiments will be conducted to determine the critical concentration of silane. The results will enable us to map conditions under which favorable heterogeneous decomposition of silane is possible.

A flow diagram (Figure 2) was prepared for the fixed-bed experiments. The necessary materials are being acquired. Gas lines, from the outdoor gas-cylinder storage to the indoor hood, were installed and pressure tested. Installation of piping in the hood has been started.

Several alternative methods for heating the fixed bed were considered. Resistance heating is thought to cause wall deposition because the wall

Figure 2. FLOW DIAGRAM FOR FIXED-BED EXPERIMENTS

temperatures are higher than the bed temperature. Capacitive heating of bed particles should work conceptually, but it may be difficult to implement in a small 1-inch I.D. fixed bed without sintering the particles. Induction heating of the bed can be accomplished if the bed particles are electrically conductive. For the initial experiments, induction heating will be tried using a bed of metallurgical grade silicon particles.

1.6.3.2 Fluidization Experiments with Inert Gas

This activity involves the continuation of experimental work from the previous phase in the following two areas:

- Capacitive heating of fluid-bed particles, minimizing particle sintering.
- Particle segregation by size with the attachment of a boot to the bottom of the fluid-bed reactor.

The first series of capacitive heating experiments was conducted with a plain stainless steel center electrode. Particle sintering was minimal (0.4% of the bed) when using large diameter particles (550 μ), but particle sintering increased to an unacceptable level (25% of the bed) when using small diameter particles (190 μ). Similar test results were obtained when using an alumina-coated center electrode. Since the electrical field length is the distance between the center electrode and the bed wall, the experiments were conducted in a fixed electrical field length. If the field length can be altered, the electrical characteristics in the bed will change and this may affect the sintering rate.

The 2-inch diameter reactor was modified to include a pyrex wall liner so that vertical path lengths could be evaluated by positioning the electrode at various heights in the bed. The field area is, however, constant since it is determined by the bed diameter. This arrangement permits control over the bed volume (field length) involved in capacitive heating.

Because the tests are of a preliminary nature, the results will not permit an evaluation of the effect of the field length on particle sintering; however, high purity silicon particles appear to sinter much less than M-G silicon particles. Complete test results will be presented in the next report.

The apparatus for particle separation experiments was assembled with a 13½-inch long boot section below the 6-inch diameter section, as shown in Figure 3. Provision was made for the periodic withdrawal of a 200 cc sample from the bottom of the boot without interrupting column fluidization. Two particle-separation tests were conducted.

In the first test, 550 μ coarse particles were successfully separated from a 187 μ bed (2.9 diameter ratio). This test used a 3-inch diameter x 13½-inch long boot section and started with a uniformly mixed bed having a 0.2 coarse fraction. Over a test period of 9.14 hours, the bed coarse fraction was reduced from 0.2 to 0.074 by the periodic withdrawal of samples from the bottom of the boot section. The average overall coarse separation rate was 352 g/hr. The maximum rate measured was 881 g/hr and occurred between 5.5 and 6.4 hours of the test period. After this time, the sample coarse fraction continually decreased until the test was terminated. For this test, the coarse to bed particle velocity ratio was 5.9 and the U/U_{mf} of the bed particles in the boot section was 3.76. The coarse particle U/U_{mf} in the boot was 0.64.

A second test was conducted to separate 427 μ coarse particles from a 187 μ bed (2.3 diameter ratio); this attempt was unsuccessful. It is not clear at this time if there is a minimum particle diameter ratio below which particle separation is not possible; however, it is probable that the boot section must be redesigned for the small diameter ratio. Modifications to the boot are presently being made to address this issue.

1.6.4 QUALITY CONTROL

For control of silane and silicon quality in the EPSDU, certain

NOTE: ALL DIMENSIONS ARE IN INCHES

Figure 3. BOOT SECTION, PARTICLE SEPARATION

analytical tests will be developed for detection of trace quantities of harmful contaminants. These tests will include methods for detecting boron, phosphorus, and hydrocarbons in silane; improved and consistent rapid electrical tests of silane purity by epitaxy; and bulk deposition of silane on a seed rod followed by float-zone leveling and resistivity profiling.

A review was conducted of the stream analyses required during EPSDU operation for data collection. These analytical requirements are in addition to the tests performed on the silane and silicon products for purposes of quality control. Based on this review, a schedule was developed listing the analyses required, streams to be sampled, and equipment and supplies necessary to perform the required tests. A total of 66 individual sample points were identified. To provide mass balance and reaction kinetic data on the reactors and the distillation columns, six points per unit of equipment will be provided with a sample volume buffer so that all six samples may be taken at one time and analyzed sequentially. Systems are being reviewed which will allow small representative samples to be taken while minimizing material loss and handling difficulties with highly reactive materials.

From the list of required analysis, existing analytical methods were identified which were most appropriate and from this list groupings were made to minimize the number of equipment items required. Finally, a proposed equipment list was developed and a preliminary laboratory layout was prepared. Basically, all major components of all streams will be analyzed by a gas chromatograph. Trace levels of gas in silane or other non-chloride containing gases will be analyzed on a second chromatograph. Liquid and solid materials will be analyzed for low ppm levels of metallic impurities by flameless atomic absorption spectroscopy. Traces of boron and phosphorus in chlorosilanes to sub-ppb levels will be analyzed by UCC's proprietary wet chemical method, using a UV spectrometer. The silicon flake will be analyzed by melting in a high-purity thin-wall quartz crucible and measuring the resistivity of the cast pellet. The slim-rod reactor, epitaxial reactor, and float zone refiner are incorporated into the facility for the determination of the silane and product silicon quality. Since the most likely form of the silicon product is a ~ 4-inch diameter rod, a core drill has been included in the equipment list so that samples can be

taken from the product ingot and zone refined prior to electrical measurements. The preliminary laboratory layout, Figure 4, shows an arrangement with a separate center section for the float-zone refiner.

1.6.4.1 Silane Analysis - Slim-Rod Deposition

A slim-rod reactor will be used to monitor the purity of silane from the EPSDU by pyrolyzing the silane and depositing silicon onto a high purity seed rod. The rod is then electrically characterized after subjecting it to a multipass zone refining step.

The most important criterion in designing the slim-rod reactor is its ability to quickly assess silane purity in a routine manner by a moderately skilled technician. The silicon deposition time must be minimized since it can be a very time-consuming operation. This indicates that a small seed rod is preferred over a large one due to essentially a fixed linear growth rate of 4 to 10 μ m per minute depending on the temperature and the reactant concentration. For example, the time required to deposit 90 percent new silicon is about 5 hours with a 2mm diameter seed rod vs. 11 hours with a 5mm diameter seed rod at a growth rate of 8 μ m per minute. The resulting rods would be 6.3 and 15.8mm diameter, respectively. Thus, the slim-rod reactor will convert a 2mm diameter x 225mm long seed rod into a 6.3mm diameter polycrystalline rod ready for float zoning. The float zoning time is also diameter-dependent. It should take under 8 hours for a standard seven-pass operation of the 6.3mm x 225mm rod.

A fast and simple operation must be accompanied by purity maintenance throughout. All hot sections of the apparatus should be constructed of low vapor pressure, non-contaminating materials. The remaining sections should be made of materials having very low affinity for sorbing gases. Thus, the reactor shell, electrodes, and reactant supply piping will be made of stainless steel, water-cooled where necessary. The chucks, which hold the silicon seed rod to the electrodes, will be molybdenum which exhibits very low vapor pressure at the expected 1000°C operating temperature, and also possesses good thermal and electrical conductivity.

Figure 4. PROPOSED EPSDU QUALITY CONTROL LABORATORY

To heat the silicon rod, a 200 volt AC power supply will be used along with a 2.5 kilowatt resistance heater in series with the rod. At room temperature, the silicon rod would have a resistance of about 24,000 Ω , while at 1200°C, the resistance would be only about 3.7 Ω . The ballast resistor would act as a current-limit to avoid melting the rod or having to rapidly decrease the impressed voltage as the rod resistance rapidly drops. After reaching approximately the operating temperature, a radiation pyrometer acting through an electronic controller and the DC power supply would maintain a precise rod temperature. The schematic for this arrangement is shown in Figure 5. An adjustable current relay on the AC power supply would provide for automatic switch-over to the DC supply. One-button system shutdown and reactor high and low pressure switches are provided for fail-safe operation. A simple thermal conductivity meter is provided to monitor the reactor exit gas composition.

Before installation, the silicon seed rod will be cleaned with an HF/HNO₃ rinse followed by a high-purity methanol rinse. The reactor system will be degassed with high vacuum followed by an H₂ etch (palladium diffused H₂) at 1200°C after the seed rod installation. During the actual decomposition, silane would be the only feed gas. Gas mixing is provided by thermal convection inside the reactor. A silane concentration of 1 to 2 percent at a rod temperature of about 850°C should provide uniform polycrystal growth at 4 to 8 $\mu\text{m}/\text{minute}$.

The design of the reactor has been essentially completed. The reactor system, Figure 6, consists of a gas feed system, reactor, and electrical power controls. The gas feed system has been designed to allow on-line control of electrical impurity concentration in the silane by a double dilution doping method. This will permit definition of the capture-efficiency of impurities by the growing silicon rod. This portion of the system will be replaced by the test gas feed system once the development activities are complete. The reactor itself consists of a 200mm diameter "bell jar" type vessel with water-cooled walls. A 2mm x 160mm rod of single crystal, modest resistivity silicon ($\sim 60 \Omega \text{ cm}$) is held vertically in molybdenum chucks connected to water-cooled stainless steel electrodes.

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LEGEND

SLIM ROD REACTOR ITEM NO. IDENTIFICATION LIST

FOR FIGURES 5 and 6

<u>Item No.</u>	<u>Description</u>
AX-1	GOWMAC Thermal Conductivity Detector
F-1	Filter, Matheson Model G134T
F-2	Filter Nupro 5 μ m sintered metal
FI-1	Flowmeter, Linde Model FM 4311-5
MFC-1	Mass Flow Controller, Linde size 10
MFC-2	Mass Flow Controller, Linde size 1
MFC-3	Mass Flow Controller, Linde size 6
MFC-4	Mass Flow Controller, Linde size 1
PCV-1	Argon Reulator, Linde Model TSA-75-380
PCV-2	Hydrogen Regulator, Linde Model UPE-30-350
PCV-3	Hydrogen Regulator, Linde Model, UPE-30-350
PCV-4	Silane Regulator, Linde Model SG-3862-350
PS-1	Pressure Switch, SPDT 1" VAC-2 psig
S-1	Control Relay, Potter & Brumfield #PM 17AY
S-2	Meter Relay w/500:5 Current transformer, GE 196 414 HFNG
S-3	Control Relay, Potter & Brumfield #PR 11 AYO
S-4	Control Relay, Potter & Brumfield #PR 7 AYO
S-5	Power Relay, Allen-Bradley #202 AC FOD 91
S-6	Argon Shutoff Solenoid Valve, normally open
S-7	Hydrogen Shutoff Solenoid Valve, normally closed
S-8	Dopant Shutoff Solenoid Valve, normally closed
S-9	Silane Shutoff Solenoid Valve, normally closed
TIC-1	Radiation Pyrometer/Controller, Ircon 2-13C10010000623
X-C-1	Programmer, XANDU UPT 100-10-X
XR-1	Recorder, Esterline Angus Model M25A01B5211
X-1	Hydrox Purifier, Matheson 8301
X-2	Oxygen Removing Purifier, Matheson 64-1025
X-3	Water Removing Purifier, Linde SG-6140-2
X-4	Hydrogen Purifier, Matheson 8363
X-5	AC Power Control, Payne Model 18D-1-40
X-6	DC Power Supply, Hewlett Packard 6469A
X-7	Electric Heating Element, Chromalox TTUH-25A

Figure 6. SLIM-ROD REACTOR SYSTEM

1.6.4.2 Silane Analysis - Direct Measurement

The analysis of silane for trace levels of hydrocarbons appears to be feasible using a reactive chromatography technique. The technique is to react to a non-volatile species essentially all of the silane sample, and then to chromatographically separate and detect the remaining compounds. Thus, using 10cc/min of nitrogen carrier gas containing 2000 parts per million of water vapor, a 0.5 cc sample of silane is injected into a 1/4-inch diameter x 6-inch long pre-column packed with Ascarite, (powdered sodium hydroxide). This oxidizes the silane only to non-volatile sodium silicate and hydroxide. The unreactive gases, chiefly hydrocarbons, are then separated in a 1/8 inch diameter by 6 foot long silica gel column and the amount is measured using a sensitive flame ionization detector. On a sample of silane, three easily identifiable peaks (methane, ethane, and propane) were detected with no interference. Although the quantitative levels of detection cannot be defined until a sample mixture of known concentration is prepared, the strength of the peak indicates that the limits will be in the low part-per-billion range. A plugging problem occurred with the Ascarite column after only 25 injections which appears related to the high humidity of the carrier gas. Resolving this difficulty and quantifying the detector response are the immediate goals.

SECTION III. CONCLUSIONS

The significant highlights and conclusions are as follows:

- Engineering activities for the EPSDU were initiated in June.
- The free-space reactor PDU is being assembled. Substantial improvements were made to the Phase II PDU so that the new PDU is expected to run for a long duration at the design throughput without the silicon powder bridging in the reactor.
- An RFP is being prepared to have a commercial vendor (s), under subcontract to Union Carbide, develop a system to melt and consolidate the silicon powder.
- A small fixed-bed apparatus is being assembled. This apparatus will be used to generate data on the critical silane concentration that separates homogeneous and heterogeneous silane decomposition, and on silicon deposition rates.
- Capacitive heating experiments show that silicon particles can be heated with minimal sintering as long as the particle diameter is large (500 μ). High-purity silicon appears to sinter much less than M-G silicon.
- Tests proved that silicon particles can be segregated by size using a boot section located below the fluid-bed reactor.
- The design of a slim-rod reactor to be used to monitor the EPSDU silane purity, is nearly complete.
- Although we have not attempted quantitative levels of detection, the analysis of silane for trace levels of hydrocarbons appears feasible using a reactive chromatographic technique.

SECTION IV. PROJECTED QUARTERLY ACTIVITIES

1.1 EPSDU - DESIGN/PROCUREMENT

- The waste burner test apparatus will be completed and the tests will be started.
- The preliminary equipment and piping layout will be completed.
- Written quotes will be obtained for most of the equipment.
- Preliminary P&I diagrams will be drawn, and the instrument and control list will be prepared.
- A definitive cost estimate of the EPSDU will be initiated.

1.6 PROCESS SUPPORT R&D

- Components for the free-space reactor PDU will be fabricated and assembled.
- The fixed-bed apparatus will be built and heating of silicon particles will begin. Tests will be started to determine the critical concentration of silane.
- Capacitive heating with minimal sintering at high temperature (800°C) will be attempted as will capacitive heating with silicon-coated electrodes.
- Particle separation tests will continue and optimum design parameters will be established.
- The melter RFP will be sent to potential subcontractors.

- Equipment procurement for the slim-rod reactor will be initiated.
- A quantitative method using reactive gas chromatography will be developed for hydrocarbon detection in silane.
- The analytical laboratory for the EPSDU will be totally defined.
- Design of the high-reliability epitaxy reactor for silane quality control will be initiated.

SECTION V. REFERENCES

1. L. M. Coleman, "Process Design Package for 100 MT/Yr Silane-to-Silicon EPSDU", Engineering Memorandum No. 6429, SGS-24, Union Carbide Corporation, June 1, 1979.