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

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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

QUARTERLY PROGRESS REPORT

JULY — SEPT 1979

UNION CARBIDE
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2009

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ABSTRACT

This report covers the work performed in July, August, and September, 1979 on JPL/DOE Contract 954334, Phase III. This phase consists of the engineering design, fabrication, assembly, operation, economic analysis, and process support R & D for an Experimental Process System Development Unit (EPSDU).

JPL and UCC agreed to a scope change in the silane pyrolysis area, whereby the EPSDU shall be equipped with melting/consolidating capacity for the full silicon output. This change is being incorporated into the engineering design.

A preliminary P & I diagram, layout, and electrical one-line were completed, and are being reviewed internally. Specifications for all major equipment were prepared and the equipment request for quotations was submitted to potential vendors. Initial vendor response, on some equipment, has been insufficient.

A small waste treatment apparatus was assembled to provide essential information for operability control system design, materials of construction, and utility requirements. Testing has recently been started. It is anticipated that this new scheme should meet all present and anticipated future environmental regulations. Much work has been done on safety and environmental considerations. Union Carbide Corporation experience is used where applicable through consultations with experts from other locations.

Major parts for the free-space reactor PDU were fabricated; they include the silicon powder hopper and the reactor top head-assembly. A detailed layout drawing was also completed which will be used during installation of valving, tubing, and instrumentation. Assembly of the PDU is proceeding well, and the checkout date in early November is anticipated.

A one-dimensional computer model of a free-space pyrolysis (plug flow model) of silane was developed and simulation runs were made. It was found

that the effects of recirculation are important and that a model capable of analyzing two-dimensional axisymmetric flows is required and is under development.

The RFP for melter subcontract was prepared and sent to six potential vendors. The subcontract will be awarded to one or two vendors who will perform a minimum amount of experimental and theoretical work necessary to design a melting/consolidation system for the EPSDU. Proposals should be in hand by early October. In order to objectively evaluate the proposals, criteria for technical assessment have been developed.

The fixed-bed experimental apparatus was assembled and is operational. It will measure silicon deposition rates and critical silane concentration in the bed at various silane concentrations and bed temperatures.

Tests continue in capacitive heating and particle separation in a fluidized bed. The bed was heated to 500°C and above for extended periods. Particle sintering can be held to a low level by maintaining a low field impedance in the bed. Particle separation tests indicate that a boot placed below the fluidized bed can be used to separate large particles. Many more tests are required, however, to optimize the boot design.

Fabrication continued on the slim-rod pyrolysis reactor for silane quality control. The laboratory room is being prepared for occupancy of the slim-rod reactor, epitaxy reactor, and float-zone machine. A preliminary design of the epitaxy deposition reactor for silane quality control was completed. On diborane analysis, a list of potential chromatographic column packings was developed based on a literature search.

SECTION I. INTRODUCTION

This report covers the work performed in July, August, and September, 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 where 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 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

1.1.1 Process Design

The process design package issued in June did not contain pipe sizing which has recently been completed. The line size selected for all major piping was determined based on the instantaneous process flow, the allowable pressure drop, and certain operating conditions, such as reduced pressure operation. The criteria considered for this determination were documented and are readily available for engineering design reference. Also, piping guidelines are being prepared to establish material requirements, wall thicknesses, connection methods, and valving desired for this program. This is being done by modifying existing UCC piping specifications, where feasible.

Review of process equipment requirements is in progress and will be completed by the end of October. Also under review are EPSDU layout, electrical power requirements and safety features.

The original EPSDU design contained only one free-space reactor and one melter which intended to process about one-fifth of the silane throughput. This was done to minimize the EPSDU cost without jeopardizing the technical success. Our reasoning was that we can learn melter performance from one melter as well as multiple identical melters. However, JPL recently made a request to melt and consolidate all silane produced in the EPSDU. A process design change notice was issued which defines the expected requirements for additional melting and consolidation facilities. For purposes of the ongoing engineering effort, special requirements, utility requirements, and building requirements will be based on one pyrolysis reactor/hopper unit and four melting and consolidation units.

A preliminary design was investigated to examine the feasibility of a packed column design for the silane column. This investigation was conducted to have an alternate design available in the event a small tray column could not meet the required cleanliness standards. Distillation column re-

quirements will be reviewed in mid-October, including technical assessment of the alternate packed bed column design for the silane column. A mini-burner PDU was built which will help determine the waste processing technique to be used in EPSDU. The burner equipment will profile a hydrogen-rich flame with quench air to optimize characteristics of chlorosilane flame hydrolysis. The burner test schematic flow diagram is shown in Figure 1. A test firing with natural gas was made in September. All necessary data should be collected in the fourth quarter, 1979.

1.1.2 Engineering Design

1.1.2.1 Controls Systems

The preliminary P & I diagram has been issued for project team review. It identifies all required process control loops. Local and panel instrument lists are being prepared, along with instrument and automatic value procurement specifications. Quality control sample points and manual valve requirements have been identified and will be added to the next issue of the P & I which presently totals 27 diagrammatic sheets. Preliminary control panel needs have been identified, including approximate dimensional (space) requirements.

A power and control wiring diagram was prepared to assist in definition, for cost estimating purposes, of electrical cable, conduit, and cable tray requirements. A second diagram will be prepared to show pneumatic instrumentation tubing requirements for the same purposes.

1.1.2.2 Layout

Layout drawings have been prepared for the East Chicago EPSDU facility site (see Figure 2) which identifies land area requirements. In addition, locations of adjacent Union Carbide facilities and expected source points and routing for all primary utilities including 6900V power, firewater header, potable water, gaseous nitrogen supply header, and sanitary sewer have been established. New stand-alone facilities will be required for gaseous argon (via liquid storage tank) and gaseous hydrogen (via either high pressure gaseous tube trailers or liquid storage tank).

FIGURE 1 BURNER TEST SCHEMATIC FLOW DIAGRAM

GD 947E

FIGURE 2. PRELIMINARY EPSDU LAYOUT

Structures and equipment drawings have been prepared for the feed/waste silicon hopper structure, the process equipment structure (reactors, distillation columns, etc.) and the pyrolysis reactor/hopper structure. Other equipment layout drawings include the pump area, compressor area, and waste burner area. The overall site drawing will be used to detail process piping, instrumentation tubing, power and signal wiring, and underground utility needs. This drawing incorporates specific environmental protection features, and safety features as further described below under Sections 1.1.2.4, Safety and 1.1.5, Environmental.

1.1.2.3 Electrical

The preliminary electrical one-line diagram was prepared and has been reviewed for first round design optimization. A maximum 2000 KVA total power requirement is anticipated, pending additional information from vendors on specific motor horsepower requirements. Additional review of emergency power requirements is required, but initial indications are that a 300 KW generator will be required to afford process safety and personnel protection in the event of a power outage. A simple pre-engineered metal building is now favored over the temporary trailer type of approach. The proposed structure would house both electrical switchgear equipment and the main operating control panel.

1.1.2.4 Safety

The safety engineer visited our Sistersville chlorosilane production facility in early September to review equipment and personnel safety practices. Additional safety provisions were defined for equipment and personnel protection. Provisions include a water deluge system for specific equipment areas where chlorosilanes are present, use of emergency trip stations for rapid process isolation and/or shutdown, and safety showers for personnel protection. Additional review will be required to establish detailed operating safety procedures for the EPSDU.

1.1.3 Equipment Specification/Procurement

1.1.3.1 Mechanical

Mechanical specifications have been prepared and requests for quotations issued for all compressors, pumps, and associated mechanical equipment. Due to unfamiliarity with process requirements, vendors appear to be having difficulty responding to our specification requirements.

1.1.3.2 Electrical

In accordance with Section 1.1.2.3 above, equipment costs have been identified. Equipment costs and needs will be refined as the electrical one-line definition firms.

1.1.3.3 Instruments and Controls

In accordance with Section 1.1.2.1 above, local and panel instrument lists are being prepared, along with associated procurement cost information. A firm equipment list will be issued pending additional P & I definition and review.

1.1.3.4 Other (Process) Equipment

Vendor responses to quotation requests have been less than satisfactory for many equipment items. Responses to all vendor quotation requests will be summarized to identify all areas where insufficient bid information exists. Alternate approaches to vendor development will be considered.

1.1.4 Installation Drawings

No activity.

1.1.5 Environmental

Cognizant state and local agencies have been identified for appro-

priate air and water permit applications during an area visit by the environmental engineer in August.

Several environmental control features were identified, primarily in the area of chlorosilane spill prevention. A channelized drainage system has been incorporated on layout drawings which features a common collection point for acid and/or chlorosilane contaminated rain, firewater and washdown water for treatment prior to sanitary sewer disposal. An air discharge process diagram has been issued to the appropriate Indiana State agency for review and comment prior to formal permit application.

1.1.6 Cost Estimate

In accordance with Section 1.1.2.2 above, EPSDU cost estimating activity has recently been initiated. It should be completed in the next quarter.

1.3 EPSDU - INSTALLATION & CHECKOUT

1.3.1 Site Evaluation

Three contractors have visited the East Chicago site to prepare quotations for soil-boring work. A contract award by October 15th is expected.

1.6 PROCESS SUPPORT R & D

1.6.1 Free-Space Reactor Development

1.6.1.1 Process Development Unit (PDU) Experiments

Fabrication of the silicon hopper (Figure 3) and the top head-assembly of the free-space reactor was completed and equipment installation is in progress. A detailed layout drawing consisting of several elevation and plan views was completed to expedite installation of valving, tubing, and instrumentation. Complete installation of the PDU and a preliminary operations manual is anticipated by the last week in October. Figure 4

FIGURE 3. SILICON HOPPER FOR FREE-SPACE REACTOR, PDU

FIGURE 4. FLOW DIAGRAM FOR SILANE PYROLYSIS EXPERIMENTS IN FREE-SPACE REACTOR

shows a simplified flow diagram for the free-space PDU.

As a safety precaution, silane will be stored outside the laboratory. Since the silane temperature will vary greatly depending on the weather, a small silane pre-heater was designed to provide the feed to the free-space reactor at a constant temperature. It consists of a 3-foot coil of stainless steel tubing, a water bath, and an electrical (Chromalox) heater.

1.6.1.2 Theoretical Analysis

A one-dimensional model of a plug-flow silane reactor was developed based on previous work done by JPL. The model was implemented as a computer program, which was checked against simple analytical solutions and verified by integral balances. Experimental evidence indicates that at temperatures below 1000°C, the heterogeneous pyrolysis of silane is limited by the surface reaction rate. Accordingly, the mass transfer limited model of the heterogeneous reaction used by JPL was replaced by a surface reaction limited model.

Simulation runs of the model were made using conditions characteristic of the free-space reactor which was tested at the Parma laboratory: silane throughput of 5 lbm/hr, inlet silane at 30°C and 20 psia, and wall temperature fixed at 750°C. The purpose of these runs was to contrast the free-space reactor against a plug-flow reactor operating at similar conditions. Several interesting conclusions can be drawn.

- In the free-space reactor, it is clear that entrainment of hot recirculating fluid by the jet is the dominant mechanism for heating the entering silane.
- The effects of the chemical reactions are negligible until the gas temperature reaches 500°C - 600°C where the reactions become very rapid and cause significant deviations in the temperature and flow fields.
- Understanding of the factors influencing the amount of recirculation is essential for successful scale-up of the reactor. Since

the effects of recirculation cannot be scaled geometrically, a model capable of analyzing two-dimensional axisymmetric flows is needed.

At throughput conditions corresponding to the Parma reactor, the heat transfer calculated by the plug-flow model was insufficient to heat the gas to reacting temperatures in a short (1 meter) tube. Either very high wall temperatures or film coefficients, an order of magnitude higher than those predicted by standard developing pipe flow correlations, were needed to get the reaction to occur. Since complete conversion of silane was observed in the free-space reactor under these conditions, it is clear that recirculation dramatically increases the amount of convective heat transfer. Both radiative and convective heat transfer are important in the free-space reactor, but the significance of the recirculation in drawing this heat into the jet axis cannot be overemphasized, so that the chemical reactions occur in the desired reaction zone.

A literature search has been performed to obtain data on the homogeneous and heterogeneous reaction rates of silane pyrolysis. The information obtained came from studies of vacuum deposition of silicon in epitaxial layers by silane pyrolysis. From theoretical kinetic considerations, it appears that the heterogeneous reaction rate data obtained at vacuum pressures must be used with caution in predicting the reaction rate at pressures near atmospheric or above. Experimental data on the reaction rates at atmospheric pressure in the temperature range between 500° to 800°C would allow the chemical kinetics to be modeled with greater confidence.

With the present rate information, it appears that the reaction is primarily homogeneous, with the nucleation primarily heterogeneous. This offers an alternative explanation as to why conversion appears poor upon start-up. The reacted silicon vapor has difficulty nucleating in the absence of recirculating particles and passes out of the reactor as vapor. It is difficult to determine whether particle growth is due to heterogeneous reaction on the particle surface or due to homogeneous gas phase decomposition followed by heterogeneous nucleation of silicon vapor on the particle. If experiments

indicate that the wall reaction and particle growth within the free-space reactor are not significant, then the heterogeneous reaction can be neglected and the analysis greatly simplified.

On September 12, a meeting with Dr. A. K. Praturi of JPL and Dr. F. M. Galloway, Jr. of Cleveland State University was held to coordinate our respective efforts on modeling of the free-space reactor. JPL is concentrating on the chemical kinetics of silane pyrolysis. They are preparing to perform experiments to determine the rate constants of both homogeneous and heterogeneous silane pyrolysis. Dr. Praturi is working to refine his plug flow reactor model to handle seeding of the reactor with hot particles. Dr. Galloway presented some comparisons of heat transfer predictions from his model with experimental data. Relatively good agreement was reported which substantiates the basic heat transfer model used. Dr. Galloway will work to incorporate particle growth into his present model.

Our current effort is in modeling the free-space reactor as an axisymmetric chemically reacting confined jet. We are formulating the governing differential equations and investigating numerical techniques of obtaining a solution to these equations. In addition, we are working to identify the important dimensionless groups in the problem, to allow for scale-up of the present reactor.

A system of five partial differential equations mathematically describe the free-space reactor: conservation of momentum (Navier-Stokes) in the axial direction, conservation of momentum in the radial direction, conservation of mass-of-silane, conservation of mass-of-hydrogen, and conservation of energy. The time-averaged form of the Navier-Stokes equations are used necessitating the selection of a turbulence model.

Several versions of TEACHT, a computer program for solving problems of steady axisymmetric turbulent flow, have been received. Test cases of a constant density isothermal fluid have been run. The results of these runs look physically reasonable and some integral quantities are conserved as required. It appears that the solutions (particularly for the pressure) are very sensitive to the number of grid points used. Large values of R/d , where

R is the radius of the duct, and d is the jet nozzle diameter, appear to aggravate the situation. Fortunately the velocity solutions are less sensitive to changes in grid size so it appears that useful test runs can be made with a relatively coarse mesh.

A version of TEACHT capable of handling non-isothermal flows has just been successfully compiled. Current attention will be focused on using this program to look at heat transfer in pipe flows, since analytic solutions and much experimental data are available for this case which will allow for checking of the computer solutions.

The problem of chemically reacting flow in a free jet has been treated by Jensen and Wilson (Combustion and Flame, 25, 43-55, 1975). Their work was based on an older program written by Spaulding's group at Imperial College that utilized vorticity and stream function as the dependent variables rather than solving for the velocities directly. Various aspects of their work should prove helpful in our modeling effort.

1.6.2 Melting/Consolidation

The RFP for the melter subcontract was prepared and submitted to six candidate subcontractors. Proposals, in response to the RFP, should be received in early October. The RFP included the statement-of-work, requirements for deliverables, terms and conditions, and instructions to bidders.

Criteria for evaluating the melter-subcontract proposals were developed. In developing these criteria, considerable thought was given to the various critical elements forming the basis for the evaluation criteria. These criteria will serve as standards for basing our decision on the subcontract award. Depending upon the relative importance of these criteria, the weighing factor to be assigned to each evaluation criterion has been identified. It is anticipated that technical evaluation should be completed by mid-November.

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.

Assembly of the fixed-bed apparatus is complete and testing has begun. Initial tests to heat a bed of particles revealed that it was not possible to inductively couple on a bed of fine particles. Therefore, the induction generator will be used to heat a metal sleeve surrounding the quartz reactor, which, in turn, will heat the bed of silicon particles.

Heating tests conducted after modifications resulted in easily obtaining desired temperatures. Two preliminary tests were run with the intention of familiarizing us with the operation of the apparatus. Both runs were made at a bed temperature of 700°C. The first was a 3-inch deep bed with 7% silane-in-hydrogen passing through the bed. The second was an 8-inch deep bed with 3% silane-in-hydrogen passing through the bed. Pictures taken with an electron microscope showed fibrous growth in both runs. The second run also showed some surface growth, but the first did not.

1.6.3.2 Inert-Gas Fluidization

Capacitive Heating of Bed

During the reporting period, many high-frequency capacitive heating tests were conducted. The bed of silicon was heated to 400° to 500°C to study the bed heating and sintering characteristics under various operating conditions.

Results are summarized in Table II. The following tentative conclusions may be made:

- Tests 12, 13, 14, and 15 established that sintering increases with load impedance.
- Tests 6, 7, 8, and 9 show that a bed having large particles sinters less.
- Tests 1 and 12 show that impurities in silicon increase sintering.
- Tests 5 and 17 indicate that coated electrodes increase sintering.

We also found that as the field length is increased, the average load impedance increases.

A high temperature capacitive heating run was conducted next, using high purity silicon particles (229 μ mean size) and a plain stainless steel electrode. A mullite liner isolated the bed from the reactor wall, except for a 1½-inch length at the bottom. The electrode tip was positioned 2½-inches above the quartz distributor. The operating conditions were:

TABLE II
CAPACITIVE HEATING TESTS

TYPE OF SILICON	TEST NO.	PARTICLE SIZE μ	LOAD IMPEDANCE Ω	POWER FREQUENCY Hz	SINTERING RATE % PER DAY	ELECTRODE
Metal- lurgical Grade	8	550	6.0	114K	1.7	Plain ↓
	1	375	4.3	15K/60K	2.0	
	10	375	25.0	15K	10.6	
	7	187	7.6	15K	91.2	
	9	550	4.2	115K	2.7	Alumina Coated ↓ Silicon Coated
	4	375	3.6	110K	51.4	
	6	187	13.6	75K/115K	63.0	
	5	375	5.8	30K/ 60K	63.9	
High Purity	13	187	3.9	15K	0.2	Plain ↓
	12	375	5.4	15K	0.5	
	15	187	7.6	15K	6.9	
	14	187	8.4	15K	11.7	
	17	187	2.8	110K	1.9	Silicon Coated

Time at temperature	15.6 hr
Average bed temperatures:	
1½ in. up	724°C
3½ in. up	863°C
5-3/4 in. up	706°C
U/U _{mf}	5
Average load power	265 watts
Average load impedance	2.9Ω
Frequency	15,000 Hz

Performance was stable on the first day and on the second day there was variation in the electrical properties indicating changing bed conditions. A high temperature excursion to 980°C also occurred when the load impedance had dropped to 1.5Ω. This was corrected by changing the electrode position and reducing the electrical power.

After cooling down the reactor, 279g of the bed was removed by vacuum extraction. This left 35g unaccounted. The removed bed contained 4.8g of sintered particles. The reactor was disassembled. The missing 35g was found as a sintered mass lining one section of the reactor wall.

The next heating test will also be at high temperature. In preparation for this test, the mullite liner has been removed and a stainless steel porous distributor has been installed. The field will be established between the electrode tip and gas distributor. Temperature profile of the bed and wall will be measured as well as the sintering rate.

Particle Separation Tests

Particle separation tests that have been conducted so far have been summarized and the summary is shown in Table III. There are 12 columns in the table which are:

Col. 1: Test Number. Some tests were restarted once or twice after

TABLE III

SILICON PARTICLE SEPARATION TESTS

IN HELIUM AT R. T. AND 1/6 ATM

Col. 1	2	3	4	5	6	7	8	9a	9b	10	11
Test No.	Time T (Hrs.)	Boot Velocity V_o (ft/sec)	Bed U/U_{mf} Column	Coarse U/U_{mf} Boot	Mean Particle Dia. Coarse Fraction $\bar{d}_{Pc}$ (μ)	Mean Particle Dia. Bed $\bar{d}_{PB}$ (μ)	Dia. Ratio $\frac{\bar{d}_{Pc}}{\bar{d}_{PB}}$	Coarse Fraction		Bed Wt. (lbs.)	Coarse Particle Separation Rate $\frac{\sum w_s(f-f_o)}{(lb/lTR)}$
								Bed f_o	Boot f		
3	0	0.39	1.5	1.0	449	218	2.06	0.25	0.25	50.8	-
	1	↓						0.25	0.25	49.6	0
	3							0.25	0.23	47.3	0
5	0	0.33	2.0	1.0	412	180	2.28	0.33	0.33	50.0	-
	1	↓						0.33	0.37	48.7	0.04
	3							0.33	0.39	46.2	0.05
8-1	0	0.48	2.0	0.9	513	216	2.38	0.61	0.61	40.0	-
	1	↓						0.57	0.98	36.8	1.56
	2.5							0.55	0.64	31.2	0.84
8-2	0	0.91	2.3	1.1	501	197	2.54	0.53	0.63	25.9	0.50
	1	↓	3.9	2.0	501	196	2.56	0.53	0.59	23.6	-
	2							0.53	0.55	21.2	0.05
8-3	0	0.39	2.0	0.8	501	196	2.56	0.53	0.53	41.2	-
	1	↓						0.52	0.69	38.7	0.31
	2				500	192	2.60	0.52	0.65	37.5	0.24
2	0	0.41	1.6	0.7	550	215	2.55	0.20	0.20	49.0	-
	1	↓						0.19	0.66	47.8	0.46
	3.25							0.17	0.68	45.8	0.44
	6.3		1.7	0.9	504	203	2.48	0.12	0.99	42.8	0.59
	6.7	↓						0.10	0.46	41.4	0.67
	9.1							0.07	0.13	36.8	0.60
4	0	0.39	2.0	0.7	550	178	3.09	0.20	0.20	50.0	-
	1	↓						0.19	0.69	48.3	0.57
	3							0.15	0.90	45.5	0.83
6	0	0.27	2.3	0.7	550	166	3.31	0.11	0.57	42.8	0.77
	1.25	↓	2.0	0.4	672	140	4.81	0.20	0.20	50.0	-
	3.25							0.18	0.56	47.9	0.55
7-1	0	0.53	4.0	0.7	672	140	4.81	0.16	0.79	45.1	0.63
	1	↓						0.06	0.98	42.5	0.86
	3		4.4	0.7	685	132	5.19	0.20	0.20	50.0	-
7-2	0	0.27	2.2	0.4	685	132	5.19	0.14	0.99	47.3	1.97
	4.75	↓						0.14	0.20	44.4	0.94
								0.05	0.81	39.2	0.67

changing gas velocities and/or adding bed particles.

- Col. 2: Elapsed time in hours after the start of the run.
- Col. 3: Boot Velocity in ft/sec. It is a superficial velocity.
- Col. 4: U/U_{mf} in the 6-inch column. U_{mf} is based on the mean particle diameter in the bed.
- Col. 5: U/U_{mf} in the boot. U_{mf} is based on the average size of the coarse particles.
- Col. 6: The average particle diameter in μ of the coarse fraction.
- Col. 7: The average particle diameter in μ of the bed.
- Col. 8: Particle diameter ratio, (Col. 6)/(Col. 7).
- Col. 9a: Coarse particle fraction in the column (bed).
- Col. 9b: Coarse particle fraction in the boot.
- Col. 10: Weight of bed particles in lbs. Samples are removed periodically during each test run.
- Col. 11: Rate of coarse particle separation in lbs/hr.

It appears after studying the data from Test Nos. 3 and 5 that the particle diameter ratio in Col. 8 must be above 2.28 for effective particle separation. Test No. 8 clearly shows that large particles can effectively be separated in a boot. After one hour of test, the boot section contained almost all (98%) coarse particles. After removal of all coarse particles in the boot, Test No. 8-1 was recreated as Test No. 8-3, but a good particle separation was not possible. This phenomenon occurred repeatedly in other test runs. At some point after the start of a test, the boot section

often contained almost all coarse particles. When the test resumed after removal of the coarse particles, we were not able to obtain a good particle separation in the boot, except in Test No. 7. At present, we are unable to explain the phenomenon.

Tentative conclusions drawn from these tests are:

- The diameter ratio (Col. 8) of at least 2.3 is required for separation.
- Coarse U/U_{mf} (Col. 5) in the boot between 0.7 and 1 is favorable. U/U_{mf} (Col 4) must not be too high. It should be below 2.
- Bed height may influence continued separation. The bed must be sufficiently high. This may explain the difference between the separation efficiencies of Test Nos. 8-3 and 7-2.

These tests were conducted with a 3-inch diameter boot section. The next series of tests will be done with a 2-inch diameter boot section. This will enable us to more independently vary the gas velocity in the column.

1.6.4 Quality Control

An Analytical and Quality Control Plan for EPSDU was prepared. This plan, covering equipment functional specifications, the sample stream flow diagram, and laboratory layout will be used to prepare detailed cost estimates and layout drawings. It also identifies the various analytical methods to be employed and provides a cross reference between the process stream, method of sampling, and the type of analysis.

1.6.4.1 Silane Analysis - Slim-Rod Reactor

Fabrication started on the slim-rod silane pyrolysis reactor (Figure 5) which will be used to convert silane into a small polysilicon rod for test and evaluation purposes. All of the component machining has been

FIGURE 5. SLIM-ROD REACTOR FOR SILANE QUALITY CONTROL

completed. Some minor delays in delivery of instruments have been encountered and are being expedited.

1.6.4.2 Silane Analysis - Direct Measurement

The development of a method for quantitative analysis of silane for parts-per-billion levels of methane, ethane and ethylene has been completed. The use of an Ascarite (powdered sodium hydroxide) column to block passage of silane followed by a silica gel column to separate the hydrocarbons has been used to chromatographically analyze silane for methane, ethane, and ethylene. The limit of detection for methane is estimated at less than 100 parts-per-billion. The trace level analysis of silane for hydrocarbons will be useful in assessing the performance of the gas stripping column in EPSDU as well as providing a means of monitoring the performance of the final silane distillation column.

Preparations are being made for developing chromatographic methods for quantifying diborane and phosphane in silane. Standard diborane/silane mixtures have been prepared for low level analytical determinations. A gas chromatograph with a thermal conductivity detector is being modified for sub-ambient oven temperature control using direct injection of liquid CO₂. High concentration (1%) diborane/silane mixtures will be used to develop the separation technique and to evaluate instrument sensitivity prior to attempting analysis of trace levels.

A literature search for chromatographic techniques pertaining to diborane has resulted in identifying four systems which have the greatest potential. Materials are being procured to prepare separation columns containing:

- 30% octoil on Celite 545
- n-hexadecane on chromasorb
- 38% mineral oil on Firebrick
- Squalane on Chromasorb W

1.6.4.3 Silane Analysis - Epitaxy

A preliminary design (Figure 6) has been prepared for a reactor system for controlled epitaxial deposition of silicon from silane onto single crystal wafers. The reactor system consists of a reactant gas metering system, an inductively heated quartz reactor, and a vacuum and vent system. The gas metering system is identical with that already being constructed for the slim-rod reactor including provision for on-line double dilution doping of the silane reactant. Solenoid valves in the gas supply lines will permit system automation for routine reproducible analytical work. The reactor itself will consist of a quartz tube with surrounding RF induction coil. A quartz boat holding a carbon susceptor at a slight angle to the flowing gas will hold two to four silicon wafers of 1 to 2-inch diameter. A special entrance arrangement will permit introducing the reactant gases, optical temperature sensing, and a means for inserting the silicon wafers. This end of the reactor will be housed inside a filtered air hood to provide a dust-free environment. Air cooling of the quartz tube will be provided to minimize silane decomposition on the tube walls. The vacuum system is provided for purging and degassing the system between runs to eliminate absorbed impurities from causing spurious results.

FIGURE 6. EPITAXY REACTOR

SECTION III CONCLUSIONS

The significant highlights and conclusions are as follows:

- UCC and JPL agreed to a scope change whereby the EPSDU will be equipped with sufficient number of melters to melt and solidify all silicon powder produced.
- A mini-burner test PDU was built, and testing has started. The PDU will be used to determine the waste processing scheme in the EPSDU.
- The preliminary P & I diagram has been completed for internal review. Other preliminary drawings completed for internal review include the layout drawing and the electrical one-line drawing.
- All major equipment specifications were prepared and requests for quotations issued. Vendor responses have been good except for a few pieces of equipment.
- Assembly of the free-space reactor PDU is progressing well. The PDU should be ready for the final checkout in early November.
- Mathematical modeling of the free-space pyrolysis indicates that the plug flow model is insufficient and also that both radiative and convective heat transfer are important. Our current effort is in modeling the free-space reactor as an axisymmetric chemically reacting confined jet.
- The RFP for melter subcontract was sent to six candidate subcontractors. We expect to receive the proposals in early October.
- Assembly of the fixed-bed apparatus was completed and testing has begun. The critical silane concentration and the particle deposition rate data will be obtained.

- High-frequency capacitive heating of silicon particles in a bed continues in order to map the operable range.
- It was shown that large particles can be separated in a boot below a fluidized bed. Parameters which seem to influence the separation efficiency include: coarse-to-bed particle diameter ratio, U/U_{mf} in bed, U/U_{mf} in boot, and bed height.
- Fabrication of the slim-rod reactor was started and will be completed next quarter.
- The development of a chromatographic method for quantitative analysis of silane for parts-per-billion levels of hydrocarbons has been completed.
- Preparations are being made for developing chromatographic methods for quantifying diborane and phosphane in silane.
- A small silane epitaxial reactor was designed. Equipment will be ordered during the next quarter.

SECTION IV. PROJECTED QUARTERLY ACTIVITIES

1.1 EPSDU-DESIGN/PROCUREMENT

1.1.1 Process Design

Ongoing review of engineering work and R & D liaison will continue, including refinements of the P & I diagram, equipment list and equipment specifications. Preliminary piping insulation requirements will be defined. Functional specifications for an alternate packed bed silane distillation column will be developed. Supporting waste burner design tests will be completed.

1.1.2 Facility Design

Preliminary layout drawings for detailed facility cost estimating definition will be finalized. Utility needs will be detailed. Soil sampling and site survey will be completed. The environmental considerations report will be issued. Definition and review of operating safety features will continue.

1.1.3 Equipment Design, Specification, Procurement

Equipment specifications will be refined and formal vendor bid offerings reviewed to permit initiation of equipment purchases after contract authorization. Detailed fabrication design of unique process equipment, including distillation columns and free-space reactor will be initiated. Equipment lists will be tabulated for detailed EPSDU cost estimating.

1.1.4 Installation Design, Specification, Procurement

Manpower and scheduling requirements will be defined.

1.1.5 Cost Estimating

The detailed EPSDU cost estimate for all current EPSDU scope-of-work activities will be finalized. Cost analysis support of facility and equipment requirements will continue.

1.2 EQUIPMENT FABRICATION AND DELIVERY

An equipment fabrication and delivery plan will be developed.

1.3 INSTALLATION AND CHECK-OUT

A preliminary installation/sub-contracting plan will be developed.

1.6 PROCESS SUPPORT R & D

1.6.1 Free-Space Reactor Development

Safety review, final checkout, and startup of the PDU will be completed. At least one preliminary run with silane will be made.

1.6.2 Melting/Consolidation

A silicon melter system subcontract will be awarded.

1.6.3 Fluid-Bed Development

Fixed-bed experiments on critical silane concentrations and silicon deposition rates will be conducted. High temperature capacitive heating and particle separation tests will be completed, and data will be evaluated. These test data will form the basis for the design of the fluid-bed silane pyrolysis system.

1.6.4 Quality Control

Fabrication of the slim-rod reactor will be completed and operation will be initiated. The epitaxy reactor will also be fabricated. Feasibility of diborane analysis by chromatography will be determined.