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DEVELOPMENT OF A POLYSILICON PROCESS BASED ON CHEMICAL
VAPOR DEPOSITION (PHASE 1)

Second Quarterly Progress Report, January 1—March 31, 1980

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SECOND QUARTERLY PROGRESS REPORT

1 JANUARY TO 31 MARCH 1980

on

DEVELOPMENT OF A POLYSILICON PROCESS

BASED ON CHEMICAL VAPOR DEPOSITION

(PHASE 1)

prepared by

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and

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May 1980

JPL Contract 955533

"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

a wholly owned subsidiary of Dow Corning Corporation

12334 Geddes Rd., Hemlock, Michigan 48626

ABSTRACT

The goal of this program is to demonstrate that a dichlorosilane-based reductive chemical vapor deposition (CVD) process is capable of producing, at low cost, high quality polycrystalline silicon. Physical form and purity of this material will be consistent with LSA material requirements for use in the manufacture of high efficiency solar cells.

The feasibility of silicon generation from dichlorosilane has been well established in the preceding quarter. A number of runs have been conducted over a broad range of conditions in an experimental CVD reactor. Silicon rods of very good surface quality and up to 42 mm in diameter have been grown in predominantly dichlorosilane-fed reactor runs. Molar silicon conversion efficiencies in excess of 45% have been observed (the projected conversion was only 35%), and unprecedented values of silicon deposition rate (high) and power consumption per kg silicon produced (low) were established for the reactor. Under comparable conditions, deposition rates and conversions for dichlorosilane runs are approximately twice those for trichlorosilane runs. Of particular importance is the fact that very few reactor-related operational problems were observed during any of the dichlorosilane runs.

Design of the Process Development Unit (PDU), whose function it will be to generate and purify dichlorosilane for feed to a production scale reactor, is complete, except for details of fire and spill protection. For these areas, additional information about combustion and hydrolytic properties of dichlorosilane is necessary.

In support of the PDU, a laboratory rearranger unit has been constructed to provide information relating to kinetics of trichlorosilane redistribution, catalyst behavior, and to allow development of reliable analytical techniques. The unit is functional, and has demonstrated that Dowex MWA-1 resin is an effective redistribution catalyst at 80°C.

A mixture of redistributed chlorosilanes from a vapor phase rearranger containing Dowex resin was fed directly into the experimental CVD reactor. The resultant polycrystalline silicon deposited was analyzed to have a resistivity of 40 ohm-cm.

Preliminary work on the EPSDU (a 100 metric ton dichlorosilane production, purification and recovery facility) has been completed, and includes a material balance for the proposed process.

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1.0 Summary

This report describes a process for the low-cost production of polycrystalline silicon from dichlorosilane via reductive chemical vapor deposition (CVD) with hydrogen. The dichlorosilane is generated from the catalyzed redistribution of trichlorosilane. The by-product silicon tetrachloride may, if desirable, be converted to trichlorosilane via hydrogenation. Objectives of Phase 1 (the current contract) are to demonstrate the feasibility of using dichlorosilane as a CVD reactor feed material and to utilize base catalyzed redistribution of trichlorosilane to produce high purity dichlorosilane. Phases 2 and 3 of the program will demonstrate the technology readiness of the process at the EPSPDU level.

A number of runs were conducted on the experimental 12" CVD reactor to establish both feasibility of silicon deposition from dichlorosilane and effective limiting conditions of operation in the reactor. Results thus far have been very promising. Silicon deposition rates and conversion efficiencies for dichlorosilane runs have been approximately a factor of two higher than for comparable trichlorosilane runs. Of particular importance were observations of conversion efficiencies of more than 45 mole % in runs 394-052-2, 394-054-4, and 394-054-3. These values substantially exceed our projected conversion efficiency of 35 mole %.

We have explored a range of operating conditions which covers factors of nearly three in chlorosilane feed rates and greater than twelve in silicon rod diameters and have experienced no difficulties in reactor operation except occasional feed condensation in a flowmeter. Silicon rods up to 42 mm in diameter have been grown with dichlorosilane feed, and have exhibited very good surface quality.

Power consumption has also been measured at the reactor. A value of 89 kwh/kg of silicon produced was determined in run 394-055-2. This value is considerably less than those encountered in standard Siemens technology, and is the lowest power consumption ever recorded in the experimental reactor.

An analytical (gas chromatographic) system attached to the reactor routinely provides detailed information on reaction by-products in the reactor vent. No unusual vent compositions relative to those in trichlorosilane technology have been observed.

In support of the PDU, whose function it will be to generate and purify dichlorosilane for feed to a production scale reactor, a laboratory rearranger unit has been constructed to provide information relating to kinetics of trichlorosilane redistribution, catalyst behavior, and to allow development of reliable analytical techniques. The unit is fully functional, and has demonstrated that Dowex MWA-1 resin is an effective redistribution catalyst at 80 °C.

A mixture of redistributed chlorosilanes from a vapor phase rearranger containing Dowex resin was fed directly into the experimental CVD reactor. The resultant polycrystalline silicon deposited when converted to single crystal silicon via float zoning had a resistivity of 40 ohm-cm.

Design of the PDU itself is complete, except for details of fire and spill protection. For these areas, additional information about combustion and hydrolytic properties of dichlorosilane is necessary. Negotiations are underway with an external laboratory to provide additional experimental hazard-related information.

Preliminary design work on the EPSDU has been completed, and includes a material balance for the entire process of silicon tetrachloride hydrogenation (to trichlorosilane), redistribution of trichlorosilane, CVD of silicon, and product recovery. The values incorporated new information from gas chromatographic sampling of the experimental reactor.

In the contract work to date, we have demonstrated that CVD of polycrystalline silicon from dichlorosilane is not only feasible, but that it proceeds smoothly over a broad range of conditions to produce high quality silicon with conversions and deposition rates substantially higher than those observed in trichlorosilane runs.

2.0 Introduction

2.1 Program Objectives

The objective of this program is to demonstrate that a chlorosilane based chemical vapor deposition (CVD) process can produce a low cost polycrystalline silicon in high volume. Product quality both in terms of purity and form should be comparable to material produced by the existing trichlorosilane CVD process which meets or exceeds requirements for use in the manufacture of high efficiency solar cells.

The overall program covers a 39 month period and consists of a feasibility phase, which is the subject of the current contract, an EPSDU design phase, and an EPSDU construction/demonstration phase. The schedule for the program is shown in Figure 1. Specific Phase 1 project objectives include:

1. Characterization of dichlorosilane as a feedstock material for an experimental CVD reactor including quantitative determination of reaction products. (CVD Reactor Feasibility)
2. Design and construction of a dichlorosilane CVD reactor which will demonstrate dichlorosilane performance in a production size reactor. (Intermediate Dichlorosilane Reactor Development)
3. Design, construction and operation of a process development unit (PDU) to characterize the trichlorosilane-to-dichlorosilane redistribution process, determine product purity, and produce sufficient dichlorosilane to permit operation of a production sized reactor. (Dichlorosilane Process/Product Evaluation)
4. Conduct preliminary design of a EPSDU based on information collected in the areas previously

described and develop supporting information for an economic evaluation of a 1000 metric ton plant. (EPSDU Design)

The general approach taken in meeting the overall program objective is discussed in Section 2.2. A brief overall process description is contained in Section 2.3. Phase 1 objectives and their relationships to each other, the EPSDU, and overall program objectives are presented in Section 2.4. Technical aspects and progress in meeting the objectives in the four basic areas are discussed in Section 3.0.

2.2 Program Approach

The low cost process for the production of high quality polycrystalline silicon via reductive chemical vapor deposition from dichlorosilane is depicted in Figures 2-3. This process consists of the hydrogenation of silicon tetrachloride to produce trichlorosilane, synthesis of dichlorosilane via redistribution of trichlorosilane, high temperature decomposition of dichlorosilane to produce polycrystalline silicon, and recovery of decomposition byproducts. Silicon tetrachloride, a major by-product of trichlorosilane redistribution and minor byproduct of dichlorosilane decomposition is recycled into the hydrogenation process. Also shown in the Figures are the distillation processes required for chlorosilane separation/ purification

The only byproduct shown as not being recycled in Figures 2-3 is hydrogen chloride. This material represents a relatively low volume stream and may be sold as a by-product although it could also be used in a hydrochlorination process to produce additional trichlorosilane.

This process addresses the shortcomings of the trichlorosilane process currently used in the production of semiconductor grade polycrystalline silicon by:

1. Use of dichlorosilane as a feed material for the CVD process. Dichlorosilane decomposes more readily than trichlorosilane, resulting in higher deposition rates.^{1,2} This behavior leads to reduced power and capital costs. Dichlorosilane also produces less vent material, thereby reducing capital associated with the recovery system.
2. Hydrogenation of tetrachlorosilane to produce trichlorosilane. This process accommodates the largest byproduct stream associated with the existing trichlorosilane-based CVD process and the largest byproduct stream of a dichlorosilane-based process. Work done at Dow Corning Corporation and by Union Carbide Corporation indicates that the hydrogenation process can produce trichlorosilane cost-effectively.^{3,4}
3. Improved CVD Reactor design. In addition to changes in CVD reactor feedstock, reactor optimization is required to further increase deposition rate and reduce power consumption. Hemlock Semiconductor Corporation, with its years of experience in reductive chemical vapor deposition using trichlorosilane as an intermediate, has developed experimental reactor configurations which should meet deposition requirements for a low cost reductive CVD process.

2.3 Process Description

2.3.1 Relevant Chemistry

The chemistry involved in the low cost dichlorosilane CVD process is relatively well established, as is the supporting technology. Basic processes required for the cost-effective production of polycrystalline silicon via the decomposition of dichlorosilane include:

Hydrogenation of Silicon Tetrachloride

Dichlorosilane Synthesis

Dichlorosilane Synthesis

Catalyst

Dichlorosilane Decomposition

The above equation is written only qualitatively since exact reaction products are temperature and composition-sensitive. Relevant points regarding the advantages and limitations of these reactions are now discussed. Since underlying chemical principles have been previously described in some detail⁹, the following discussion will be kept brief.

HYDROGENATION OF SILICON TETRACHLORIDE

The substantial amount of silicon tetrachloride which is generated in the redistribution and decomposition processes requires a means of recycling the material and/or converting it into a more useful material. Such reactions will not be explored under this contract; however, Union Carbide Corp. has demonstrated the feasibility of producing trichlorosilane from hydrogen/silicon tetrachloride mixtures in a high pressure silicon fluidized bed operating in the vicinity of 500 °C.⁴ Efforts in the hydrogenation area by Hemlock Semiconductor are not warranted until reactor/reactant feasibility has been established and applicability of the UCC hydrogenation process to this project is established.

DICHLOROSILANE SYNTHESIS

Considerable experience at Dow Corning⁵, Union Carbide Corporation⁴ and elsewhere has demonstrated the preferred route to dichlorosilane to be the acid/or base-catalyzed redistribution of trichlorosilane

catalyst

A wide variety of species, including ammonium salts, free amines, phosphonium salts, phosphoramides and aluminum chloride have been shown capable of catalyzing redistribution reactions under mild conditions.

The need in the present program is for a solid, nonvolatile catalyst capable of inducing a redistribution reaction at reasonable rates while occurring at moderate temperatures and, preferably, for both liquid and vapor trichlorosilane feed. Workers at Union Carbide have demonstrated that an amine-functional organic polymeric resin will catalyze redistribution of chlorosilane mixtures at temperatures between 50-80 °C. A similar basic resin Dowex MWA-1, manufactured by Dow Chemical Corp., has been chosen as the catalyst for our system.

Equilibrium relationships among chlorosilanes are known from research conducted at both Dow Corning⁶ and Union Carbide⁴. A fully equilibrated system at 80 °C with a Cl/H ratio of 3 (pure trichlorosilane as reactant) should consist of ca. 11% dichlorosilane, 12% silicon tetrachloride, <1% monochlorosilane, with the balance being trichlorosilane. Since the reaction is nearly thermoneutral, the temperature dependence of the equilibrium position is slight.

REDUCTIVE CHEMICAL VAPOR DEPOSITION VIA DICHLOROSILANE

The principal advantages of dichlorosilane with respect to trichlorosilane for reductive chemical vapor deposition of silicon are three: its relative instability both thermodynamically and kinetically, and its lower chlorine content.

In thermodynamic terms, dichlorosilane is a substantially better source of silicon than is trichlorosilane. For instance, at 1070 °C and 7 mole %, equilibrium conversions of trichlorosilane and dichlorosilane into silicon are, respectively, 40% and 65%⁶.

Moreover, because of its lower chlorine content, dichlorosilane is less susceptible than is trichlorosilane to conversion decreases as its molar percentage in the CVD reactor feed increases. At 14 mole %, for instance, the equilibrium conversions to silicon are 58% and 31% for dichlorosilane and trichlorosilane, respectively.

Since equilibrium conditions do not in fact prevail in CVD processes anticipated for application in this program, the above equilibrium relationships will be modified by kinetic realities. Several investigators have demonstrated that, under conditions used for epitaxial deposition, formation of silicon from dichlorosilane is characterized by a lower activation energy than corresponding formation from trichlorosilane.^{1,7,8}

Additional support for closer approach to equilibrium in dichlorosilane systems comes from Union Carbide patents² which claim conversions into silicon of up to 60% in a single rod CVD reactor.

The effect of kinetic behavior is therefore to enhance the thermodynamic advantage of dichlorosilane over trichlorosilane for silicon manufacture.

The lower molar chlorine content of dichlorosilane than trichlorosilane has a beneficial effect on the amount of byproduct chlorosilane which must be recirculated or otherwise accommodated in a polycrystalline silicon CVD process. Not only will the weight of chlorosilanes in reactor vents be lower when dichlorosilane is utilized, but the distribution of these byproducts will be more favorable. The present process based on trichlorosilane generates substantial quantities of silicon tetrachloride; with dichlorosilane as a feed material, the principal CVD reactor byproduct should be trichlorosilane. This assumption has been borne out in gas chromatographic analyses of runs on the experimental reactor.

2.3.2 Process Implementation

Implementation of the low cost chlorosilane based CVD process is illustrated schematically in Figures 2-3.

Hydrogenation of silicon tetrachloride occurs in a fluidized bed reactor. The fluidized bed is made up of finely ground metallurgical grade silicon fluidized with a H_2/SiCl_4 gas stream. The hydrogenation product (H_2 , HSiCl_3 and SiCl_4) is first stripped of hydrogen and any highly volatile impurity species. The bottoms material from this first separation feeds a second distillation column where the trichlorosilane-silicon tetrachloride separation is accomplished. Silicon tetrachloride is returned to the fluidized bed reactor while the purified trichlorosilane is fed into a redistribution column for dichlorosilane synthesis. Output of the redistribution column contains approximately 11 percent H_2SiCl_2 along with H_3SiCl , HSiCl_3 and SiCl_4 , with HSiCl_3 representing the bulk of the chlorosilane present in this stream (approximately 80 percent). Dichlorosilane separation is effected by a second distillation process and taken off the distillation column as an overhead stream. The bottoms from this distillation column are recycled into the HSiCl_3 - SiCl_4 distillation column.

Dichlorosilane is vaporized and, along with hydrogen, is introduced into a polycrystalline silicon CVD reactor where it is decomposed on a resistively heated substrate. Reaction products are collected and processed through a recovery system which serves to remove and purify the hydrogen for recycle to the CVD reactor and separate chlorosilanes in the vent stream from the HCl . The recovered chlorosilanes are introduced into distillation column 3 where they begin the recycle process either forward to the reactor (H_2SiCl_2) or back to the H_2SiCl_2 synthesis and SiCl_4 hydrogenation segments of the process.

The process is characterized by nearly complete chlorine and hydrogen recycle. Chlorine loss occurring as HCl at the output of the recovery system is made up by the addition of SiCl_4 into the fluidized bed reactor. If HCl generation becomes excessive, the material can be recycled by conversion into trichlorosilane.

3.0 Technical Status

Phase 1 technical efforts are limited to the four areas discussed in Section 2.1. No efforts are being expended in the area of silicon tetrachloride hydrogenation due to JPL support of the Union Carbide program. Neither are efforts being devoted to the development of CVD reactor vent product recovery technology. This technology is closely aligned with recovery system technology currently employed in the trichlorosilane CVD process. Phase 1 efforts thus consist of the following:

- CVD Reactor Feasibility
- Intermediate Dichlorosilane Reactor Development
- Dichlorosilane Process/Product Evaluation
- EPSDU Design

A milestone chart detailing work to be accomplished in these four general areas is shown in Figure 4. These four major areas of technical activity are discussed in Sections 3.1 through 3.4.

3.1 CVD Reactor Feasibility

3.1.1 Objectives

The objectives of the reactor feasibility task are to:

1. Establish feasibility of dichlorosilane as a feed material in a high deposition rate CVD reactor.
2. Optimize reactor operating parameters for dichlorosilane feed.
3. Develop comparative data regarding dichlorosilane and trichlorosilane behavior in an experimental CVD reactor.
4. Provide necessary information for scale-up to an intermediate size or full-scale production reactor.
5. Establish vent product composition to permit 1000 metric-ton plant design and costing.

6. If necessary, evaluate the performance of a reactor operating on mixed feed (dichlorosilane and trichlorosilane).

The reactor and support systems employed in this experimental program are described in Section 3.1.2, while experimental results are presented in Section 3.1.3.

3.1.2 Experimental CVD Reactor

A small existing experimental reactor, designated for purposes of this report as reactor 394, is being used in this program to permit the accelerated pace of Phase 1. The reactor is equipped to monitor chlorosilane composition in both feed and vent lines to permit accurate determination of vent product composition required for EPSDU design.

The reactor is supplied from a manifold which permits pure dichlorosilane, pure trichlorosilane, or a combination of the two to be mixed with hydrogen in any desired proportion and fed to the reactor. In addition, the effluent from a vapor phase rearranger, packed with Dowex MWA-1 resin, can be passed directly into the reactor. Analytical support for both reactor feed and vent streams and the rearranger is provided by a gas chromatograph which is linked to a remote microcomputer-based data processing system.

Electronic grade dichlorosilane is purchased in 50 or 250 pound cylinders from a commercial supplier and is used as the source of the dichlorosilane for experimental runs. The cylinders are heated to maintain an adequate vapor pressure of dichlorosilane.

The reactor, rearranger and their supply and support systems are discussed in more detail in the first Quarterly Report.⁹

3.1.3 Experimental Results

The majority of dichlorosilane CVD runs made to date have been "segmented"; that is, silicon rods have been grown to a

certain diameter using trichlorosilane, the run interrupted and rod diameters measured, then the run resumed with dichlorosilane feed. This approach provides useful information related to dichlorosilane reactor behavior, while conserving dichlorosilane--a rather expensive commodity. There is no evidence to date that reactor behavior is influenced by the growth history of the silicon rods.

Data Review/Revision. A comprehensive review of previous reactor data was undertaken. Previously reported values of silicon feed rates were modified to reflect new information from Matheson Co., the manufacturer of the rotameters on the experimental reactor, on non-linear behavior of the meters. Other minor corrections on previously measured feed flow rates have also been made, and are included in the values presented in this report.

Revisions in values for the amounts of silicon deposited were also necessary. Both volume calculated (from rod diameters) and scale weights were employed as measurement techniques. A more precise and consistent volume-calculated method for determination of silicon deposition weights has now been adopted, and all prior values revised.

The net effect of the corrections to previously reported data is to increase the dichlorosilane-to-silicon conversion by an average of 8% (that is by a factor of 1.08).

Trichlorosilane reactor behavior. During the last quarter, run segments have been made with both pure trichlorosilane and dichlorosilane as feedstocks. Table I is a summary of reactor performance with trichlorosilane feed. Runs 394-053-1 through 394-060-1 were completed this quarter and can be compared with runs conducted previously. Comparative data are most meaningful when runs are made with comparable silicon rod diameters and feed rates.

Several trichlorosilane segments have been conducted at silicon feed rates of 299 g silicon/hr. Table II is an excerpt

of Table I which includes only runs at this feed rate. Several qualitative relationships are apparent from the Table. Segment 394-053-1 is a small diameter run which afforded a 14.6% conversion into silicon. Such low conversions are typically experienced under surface area-limited conditions. The four segments in the middle of the Table featured a diameter range of about 3-23 mm, and were conducted to assess consistency in measured reactor performance. Reproducibility was judged to be quite good: deposition rates for the four runs were calculated to be $.344 \pm .016$ g/hr/cm.

The last two segments in the Table were conducted at considerably larger rod diameters; the additional surface area available for reaction results in higher conversion values and deposition rates.

The effect of increasing trichlorosilane feed rates can be appreciated from Table I. Under otherwise comparable conditions, when feed rates are increased, % conversion decreases but, due to the higher throughput, deposition rates increase.

Dichlorosilane reactor feasibility. Table III summarizes results of reactor performance using dichlorosilane as feedstock. As previously discussed, these runs were normally continuations of prior trichlorosilane runs (those represented in Table I). Segments 394-053-2 through 394-059-1 were completed this quarter. For several of the runs, conditions were selected which were considered demanding. The expectation was that, at high feed rates and/or large rod diameters, operational problems such as vapor nucleation or bell jar deposition, or a significant loss in surface quality of the silicon would be apparent. However, no such operational problems have been experienced. Vapor nucleation--formation of silicon "dust" particles--has not been observed, and jar deposition has been slight, and quite comparable to trichlorosilane runs. Moreover, silicon surface quality has remained consistently high, as can be judged from the rod section from run 394-056-4 shown in Figure 5.

The data listed in Table III indicate the same qualitative relationships observed for trichlorosilane systems are valid for dichlorosilane: conversion increases with rod diameter and decreases with feed rate, whereas deposition rate increases with both rod diameter and feed rate.

Conversion for many of the runs exceeds the target figure (contained in the original Hemlock Semiconductor proposal) of 35% for this project. The deposition rate of 1.67 g/hr/cm in run 394-055-6 is the highest yet observed in this reactor.

Power consumption measurements have also been made for dichlorosilane run segments. The power figures, expressed as kwh/kg silicon produced, indicate that, as expected, power requirements depend both on rod diameter and deposition rate. At constant deposition rate, power usage will increase with rod diameter, since reaction occurs on the substrate surface, but the entire volume of the rod must be heated. Power consumption per kg silicon deposited will naturally decrease as deposition rate increases. The situation is in fact somewhat complicated by the fact that rod diameter and deposition rate are positively correlated.

Runs 394-056-2 and 394-057-2 were conducted with low feed rates in hopes of obtaining unusually high conversions. Although the values observed were reasonably high for the rod diameters present during the run, the results suggest that, even for low feed rates, conversions greater than about 35% can only be attained at rod diameters in excess of approximately 30 mm. Rod diameters considered typical for a production process would be in the 80 mm - 140 mm range.

Starting with run 394-056-3, a 250 lb cylinder was used as the source of the dichlorosilane. Once the additional heating required for the cylinder was accommodated, the new dichlorosilane feed system functioned well, except as noted below.

Segment 394-056-4 was a repeat of the conditions of 394-055-6, to verify the high deposition rate for the earlier run. The conversion and deposition rate for the run were only

slightly lower than before, and the diameter of the rods--42.3 mm--is the greatest of any yet grown with dichlorosilane. Rod surface quality was good, and silicon deposited on the jar was judged to be less than .5 mm thick.

In run 394-057, silicon in each of the three segments was grown entirely with dichlorosilane. Rods were grown at moderate feed rates up to 29 mm in diameter. There were no operational problems associated with the reactor during any of the segments, except for brief periods of condensation in the feed flowmeter, as discussed below. The data and observations from run 394-057 verify our contention that segmented trichlorosilane/dichlorosilane runs are good simulations of runs grown entirely from dichlorosilane.

Experimental Problems. At the onset of a run--for both dichlorosilane and trichlorosilane--there is a tendency for the chlorosilane vapor to liquefy in the flowmeter used to measure feed flow rates. This is to a large extent a seasonal problem associated with the experimental arrangement. The temporary solution is to bypass the reactor until the stream revaporizes; the flow normally then remains stable for the duration of the run. A longer term solution will be to heat trace the flowmeter. This modification will soon be implemented.

During the course of a dichlorosilane segment (394-059-1), the liquid level in the cylinder became rather low, and a substantial amount of heat was transferred through the cylinder walls to a fusible link on the top of the cylinder (rated at 73 °C). The link melted and exposed a second frangible, a rupture disk rated at a pressure of 250 psig, to the contents of the cylinder. Since the cylinder pressure was far lower than the rated pressure, the rupture disk should have held and permitted continued operation. However, the disk leaked, necessitating removal and disposal of the cylinder. Further activity in the experimental reactor was temporarily suspended and a modified heating system was installed while awaiting delivery of a new dichlorosilane cylinder.

Silicon Purity Data. Most of the silicon rods grown during this quarter have been too large to be analyzed for purity via our Quality Assurance department's standard zone refining technique. However, a 17 mm rod from run 394-058-1 was assayed for electronic impurities by a 7-pass zone refining procedure, with results as presented in Table IV. The level of boron is compatible with semiconductor grade material. The concentration of donor atoms is, however, higher than semiconductor industry standards. This situation can be attributed to unfortunate timing: the reactor vent had been disassembled, cleaned and reassembled just prior to the run. Such a procedure invariably generates high donor levels in the run. It should also be noted that since the dichlorosilane used was not manufactured by HSC, we have no control over the purity of the material.

The vapor phase rearranger run, described in section 3.3.2 generated silicon which was also subjected to quality analysis. In this instance, the feedstock was HSC semiconductor grade trichlorosilane. Data from 7-pass zone refining analysis are provided in Table IV. The data indicate that, even with a relatively new apparatus (which will lead to abnormally high levels of donor), the boron and donor levels are consistent with semiconductor quality. Our interpretation is that, under the conditions of the run, Dowex resin does not seriously contaminate chlorosilanes with electronically active impurities.

Gas Chromatographic Data. Figure 6 represents relative concentrations of by-products in the reactor vent during run 394-057-5. The figure indicates the high reproducibility of the analyses and that at relatively large diameters most of the dichlorosilane not converted into silicon is transformed into trichlorosilane. Under the conditions of this run, the vent composition is not greatly dissimilar to that of a corresponding trichlorosilane run.

3.2 Intermediate Reactor Development

3.2.1 General

Correlations are currently being developed which will allow accurate extrapolations of performance in the 12" experimental reactor to larger production reactors. These correlations are based on existing trichlorosilane data and will be finalized during the next quarter.

Much of the scheduled activity in this task involved design modification of existing (trichlorosilane) production reactors to accommodate dichlorosilane feed. However, the nearly complete absence of reactor-related operational problems encountered with dichlorosilane in the experimental reactor to date has made activity in this area unnecessary. Indeed, discussions are underway with JPL personnel regarding acceleration of this task by feeding a standard production reactor with commercially purchased dichlorosilane. Engineering design work in support of a production-scale dichlorosilane reactor feed system has been initiated, and should be completed in the next quarter.

3.3 Dichlorosilane Process/Product Evaluation

3.3.1 General

The objectives of this task are:

1. Establish purity of dichlorosilane produced via catalyzed redistribution of trichlorosilane.
2. Permit characterization and optimization of the redistribution process through design, construction and operation of a process development unit (PDU) and provide design information for the EPSDU and 1000 metric ton plant.
3. Provide sufficient dichlorosilane at a reasonable cost from the PDU to permit regular operation of an intermediate size CVD reactor at high feed rates.

These objectives will be met through dual tasks designed to provide a data base for PDU design and operation, and actual PDU design, construction and optimization. The PDU support effort is discussed in section 3.3.2 while PDU design is considered and reviewed in section 3.3.3.

3.3.2 PDU Support

General. The overall objective of the PDU Support laboratory program is to provide data to support the design, understanding and safe and efficient operation of the dichlorosilane mini-plant. The chemical reactions and principles of operation of this plant are described elsewhere. Information is needed the following general areas:

- Process Stream Analysis
- Catalyst Stability
- Redistribution Kinetics
- Product and Process Stream Safety

A discussion of the objectives and approach in each of these areas follows:

Process Stream Analysis. In order to monitor and control the mini-plant process some form of liquid product stream analysis is desirable. The simplest method is gas chromatography (GLC). Besides the basic GLC equipment, information on the detector response factors for the various chlorosilanes, in particular, dichlorosilane and monochlorosilane, and a method of sampling the pressurized liquid process chlorosilane streams are required.

The approach to instrument calibration has been to prepare calibrated gas mixtures of the chlorosilanes via conventional vacuum line techniques, inject these into the gas chromatograph and compare peak areas relative to trichlorosilane to obtain the necessary detector response factors.

The approach to process stream sampling is to determine the feasibility of the following techniques and select the most favorable.

- 1) Direct syringe injection of the liquid chlorosilanes into the GLC.
- (2) Injection of the liquid chlorosilanes into the GLC via an automatic liquid sampling valve.
- (3) Flash evaporation of the liquid chlorosilanes with subsequent gas injection into the GLC.

Catalyst Stability. Since the solid catalyst used to effect the redistribution of trichlorosilane, Dowex MWA-1 Ion Exchange Resin, is an organic aminofunctional material, there is some question as to its thermal stability. Of particular concern is the extent to which the material loses nitrogen and whether this nitrogen is in a reactive form, such as an amine, which might cause unwanted redistribution during the distillation and storage of dichlorosilane.

The experimental approach is to subject the Dowex resin to temperatures in excess to those practical for the redistribution section of the mini-plant, e.g. 150-200 °C, and determine what and how much material is liberated. Conventional vacuum line techniques in combination with infrared analysis will be employed for characterization.

Product and Process Stream Safety. Although data are available concerning the hazards and precautions for silicon tetrachloride, trichlorosilane, dichlorosilane and silane, very little is known about monochlorosilane. There is concern that small amounts of monochlorosilane (and silane) formed via direct redistribution (or in storage if active decomposition products of Dowex resin are present) may present a distinct safety hazard. Although some relevant information can be obtained from the relatively small amounts of materials being handled in the above laboratory programs, the Dow Corning Corporate Safety Department will be involved in suggesting further tests and operating requirements.

Redistribution Kinetics. Because of the safety concerns expressed in the preceding section, and to simplify the PDU design principles previously described, it appears desirable to use a reactant feed mixture composed of 80% trichlorosilane and 20% silicon tetrachloride in order to suppress the formation of monochlorosilane and silane. Information on the kinetic behavior of this mixed feed system is not available at this time. A laboratory scale redistribution unit has been designed and constructed to obtain this essential information and extend the available kinetic information on a pure trichlorosilane feed system to higher liquid flow rates. It will also be possible to assess product purity by depositing a silicon evaluation rod from the material produced by this laboratory unit.

Laboratory Rearranger Unit.

The laboratory scale redistribution unit has been designed and constructed and is shown schematically in Figure 15. The unit consists of a manifold which includes two stainless steel sample cylinders and a small rearranger. One of the cylinders is used to feed pure trichlorosilane or mixed feeds of trichlorosilane and silicon tetrachloride to the rearranger. The other cylinder is used to collect effluent from the stainless steel tubing which will be immersed in an oil recirculating bath to insure constant temperature operation. Provisions exist for removal of samples for analysis (by gas chromatography), waste removal, and automatic venting to a purge line under upset conditions. The apparatus is designed for manipulation of liquid streams, but can also be adapted for vapor phase operation.

RESULTS OF EXPERIMENTAL WORK

Process Stream Analysis. The Varian Model 3400 gas chromatograph arrived and was installed during this quarter. A Valco automatic gas sampling valve was field installed. The unit has been fully checked out with various chlorosilane mixtures and the procedures for analyzing these mixtures established.

Column technology is complete. An OV-101 on Chromosorb W.H.P. column was found to quantitatively and reliably separate the chlorosilanes (see Figure 9). Response factors for the chlorosilanes have been determined from calibration samples.

Catalyst Stability. Most of the work on basic properties and thermal stability of Dowex resin has been completed and reported previously. During this quarter one series of experiments was undertaken to determine if gross distortion of the Dowex particles occur when subjected to various external loading pressures. Samples of Dowex resin were heated for one-half to one hour at temperatures to 129 °C and pressures to 32

psig in a hydraulic press type unit and examined microscopically following the heat/pressure cycle. No gross distortion of the Dowex particles was noted at 60X magnification.

Redistribution Kinetics. Laboratory Scale Redistribution Reactor Unit

Construction of the laboratory unit (see Figure 8) is complete. The unit has been approved by the Safety Audit team, and the operating procedure for this unit has been written. Operation of unit has been checked out with silicon tetrachloride and no operational difficulties were encountered. Kinetic experiments with pure trichlorosilane and trichlorosilane/silicon tetrachloride mixtures should commence in the near future.

Static Catalysis Experiments

While construction of the laboratory scale redistribution unit was in progress some static catalysis experiments with Dowex resin were conducted. These experiments were especially useful in evaluating gas chromatographic procedures. Major results of these experiments are presented in Table V.

The data indicate attainment of full equilibrium among the chlorosilanes for each of the mixtures, demonstrating that the Dowex resin is an effective catalyst under these conditions, and verifying the reliability of the analytical techniques.

D. Product and Process Stream Safety

Materials Safety Data Sheets on the materials involved in the DCS Intermediates process have been assembled, distributed and reviewed with the personnel working on this project.

Several minor explosions were experienced during handling of dichlorosilane on the vacuum line unit interfaced with the rearranger unit during the static catalysis experiments described above. The cause of these explosions was traced to a leaking gasket on the exhaust side of the vacuum pump. The exhaust vent of the vacuum pump is argon purged and only minimal quantities, i.e. <1gm, of chlorosilane are allowed to pass directly through the pump. Apparently a small amount of air was able to enter the head space above the vacuum pump oil through the faulty head gasket and form an air-dichlorosilane mixture which exploded. Although these explosions (or rapid deflagrations) were not serious in nature, they are of concern.

3.3.3 Process Development Unit Design

The PDU design selected is represented in Figure 10. The design features a mixed trichlorosilane/silicon tetrachloride feed to the rearranger which, according to estimated thermochemical data, should largely suppress formation of monochlorosilane and silane. Elimination or suppression of monochlorosilane is deemed desirable at the PDU stage because of potential difficulties with handling the material and its possible vapor nucleation in a CVD reactor.

The single still in the system will be used to purify dichlorosilane and, as the last stage in a production cycle, to distill a trichlorosilane/silicon tetrachloride mixture to provide feed of appropriate composition for the next run. Proposed operating sequences for the unit were provided in the first quarterly report.

Design of major equipment for the unit is complete, and quotations from vendors solicited. The dichlorosilane storage tanks have been reduced in size to a total storage of 50 gallons due to fire and explosion considerations. The Hemlock location known as S-22 has been selected as the location for the plant. Preliminary design of equipment layout has been completed. The one design element which remains uncompleted is the hazard-related area of fire and spill protection. As

discussed below, we feel additional information is necessary in this area.

PDU sizing was based on a 35 lb/hr production rate of dichlorosilane. This rate requires 1085 lb/hr of feed whose composition is 80% trichlorosilane and 20% silicon tetrachloride.

The two major pieces of equipment in the PDU are the still and redistribution reactor (rearranger). The still was designed for a reflux ratio of 15:1, and 20 theoretical trays. This design will yield an overhead product with approximately 99% dichlorosilane (including any monochlorosilane present) and 1% trichlorosilane. Goodloe* packing was selected because the height equivalent to a theoretical tray was evaluated to be considerably lower than for other packings considered.

The reactor was sized for liquid phase operation with a 30 minute residence time at a 9.0 ft/hr velocity. Based on the redistribution data presented in Ref. 4, these operating conditions should be adequate to attain 90% of equilibrium at 65 °C, assuming that Dowex MWA-1 resin is at least as effective as Amberlyst A-21.

Product Safety--Handling of Dichlorosilane. During the last quarter, the literature relating to combustion and hydrolytic behavior of dichlorosilane was carefully reviewed. Several sources indicate that, under some conditions, dichlorosilane/air mixtures spontaneously and violently explode at room temperature. These reports are difficult to reconcile with the literature value for autoignition temperature of 100 °C. Other accounts have described dichlorosilane/air ignition events as unusually forceful. Our own recent experience with ignition of dichlorosilane has been described earlier in this report.

Little has been reported on interaction of dichlorosilane and water; there are indications that dichlorosilane can ignite when the material contacts a small amount of water, and that unstable, shock-sensitive polymers of approximate composition

$(\text{SiH}_2\text{O})_x$ can be formed from hydrolysis of dichlorosilane.

To assure adequate design of fire and spill protection, a decision on required data was made with the help of Dow Corning Corporation's Safety and Loss Prevention department. We plan to have an outside laboratory perform a series of tests to establish autoignition temperatures, explosion severity, and hydrolytic behavior. Their findings will be accompanied by recommendations for equipment separation, fire protection, spill protection, and emergency vent discharge requirements.

3.4.0 Preliminary EPSDU Design

3.4.1 General

The time constraint of demonstrating technology readiness in a 39 month program requires preliminary EPSDU design to be completed within the Phase 1 time frame. Mass balance will be completed based on available data regarding the hydrogenation process and dichlorosilane synthesis coupled with data generated in task 3.1 regarding deposition rate and CVD reaction products.

The EPSDU will consist of the following processes:

- dichlorosilane synthesis and purification
- polycrystalline silicon CVD using dichlorosilane
- vent product recovery

Trichlorosilane produced by existing process streams will be used as feedstock for dichlorosilane synthesis and silicon tetrachloride will be disposed of in the manner currently employed by Hemlock Semiconductor. Demonstration of the hydrogenation process is being undertaken by Union Carbide Corporation under a separate JPL contract.

3.4.2 Status

Mass balances presented in the first quarterly report have been modified using GLC-based vent gas composition data obtained in the experimental 12" reactor. The revised flows are shown on figure 11.

Figure 11, combined with table VI, indicates flows in pounds per hour for each pound-mole per hour silicon production. These flows assume no material losses, which is justifiable as there are no waste streams involved. This portion of the system has been computer modeled, allowing material flow and composition to be determined for various silicon production rates and decomposition reactor vent gas compositions.

With respect to figure 11, trichlorosilane enters at line AA, and is stored. The trichlorosilane will be pumped through the feed heater and redistribution reactor, which will be sized to allow sufficient reaction so that stream AD is 10% dichlorosilane. This material will enter the dichlorosilane still concurrently with chlorosilanes from the recovery area, (stream AE). Stream AD contains approximately 12 times the material of stream AE. More economical operation of the column would likely result if a single feed point were employed, as indicated in line AF.

The overhead of the dichlorosilane still will be controlled to allow trichlorosilane and monochlorosilane to be taken off in equal percentages (estimated to be ca. 4% each), with the remainder being dichlorosilane. The dichlorosilane is stored until used in the decomposition area. The bottoms from the dichlorosilane still contain trichlorosilane and silicon tetrachloride, along with traces of dichlorosilane. The bottoms are sent to the trichlorosilane still, where trichlorosilane is taken off overhead to supply the redistribution reactor, and silicon tetrachloride is removed from the still bottom and sent to the (presently existing) main HSC recovery system for processing.

The decomposition reactor vent gas has an estimated composition (excluding hydrogen) of 20% dichlorosilane, 53 % trichlorosilane, 14% silicon tetrachloride, and 13% HCl. This material is admitted to the recovery area, where hydrogen and HCl are separated from the chlorosilanes. Hydrogen is recycled

back to the decomposition reactors and HCl is returned to the main HSC recovery system.

Energy balances have not been undertaken for the recovery or dichlorosilane production units at this time. This activity will require a more detailed design of the various unit operations. That design will also serve as the basis for equipment cost and operating expenses.

Various recovery designs are currently under consideration, and unit operations and flows are being defined. Although design features could change slightly after data are received from a production scale operation, comparison of various systems using current data should allow adequate processing selection. A recovery system for a plant based on dichlorosilane feed will be similar to that appropriate for a trichlorosilane-based plant. Since the conversion efficiency for silicon production from dichlorosilane is roughly twice that for trichlorosilane, the recovery system for a dichlorosilane plant will be about half the size of a trichlorosilane plant at the same production level. Detailed discussion of the proposed dichlorosilane recovery system is not possible, since proprietary information is involved. However, the facility would be rather similar in design to that published by Yaws* as being typical for Siemens silicon technology.

FUTURE ACTIVITIES

Final unit operation selection and proper interconnection of the dichlorosilane production/purification facility with the recovery system is expected in the next quarter. This will be followed by final flow sheets which will include mass and energy balances. Initial equipment costing will include only major equipment purchases such as distillation, tankage, heat exchangers, pumps, reactors, and compressors.

A preliminary estimate for a 1000 metric ton plant should be completed during the next quarter.

4.0 Conclusions and Recommendations

Over a range of CVD reactor operating conditions conducive to high silicon deposition rates and/or high conversion efficiencies, dichlorosilane-fed systems generate high quality silicon smoothly and reliably. No serious operational problems such as excessive deposition on bell jars were encountered. Both deposition rates and conversions are approximately twice those of comparable trichlorosilane runs.

Preliminary results with the chosen redistribution catalyst, Dowex MWA-1, indicate acceptable catalytic activity under projected operating conditions of the rearranger unit.

A relatively simple single still design has been chosen for the PDU. Process design is complete except for fire and spill protection features, which will necessitate additional (and external) experimental information, and likely cause some delay in the construction of the unit. Major pieces of equipment have been designed and submitted for final vendor quotations.

Except for the safety-related delay in finalizing PDU design, the program is proceeding on plan. Because of the highly encouraging results to date in the experimental reactor, it may be possible to circumvent the earlier portions of Task 2 (intermediate reactor development), and feed commercially purchased dichlorosilane to a production reactor of current design. Such a possibility is being discussed with JPL personnel.

5.0 Program Schedule/Plans

Except as noted above (PDU construction), the program is proceeding according to or exceeding plan. Efforts planned in the various task areas in accordance with the Program Schedule shown in figure 1 are summarized below.

1. Reactor Feasibility (3.1)

Formulate and implement strategy for optimizing reactor decomposition conditions for experimental reactor.

Establish correlations of time-dependent parameters (e.g., vent composition) with reactor conditions.

Determine validity of scale-up parameters for use in extrapolation from reactor 394 to a production scale reactor.

2. Intermediate Dichlorosilane Reactor Development (3.2)

Identify operational parameters required to demonstrate a high deposition rate consistent with EPSDU requirements.

Ascertain feasibility of utilizing unmodified (HSC) production reactor for this task.

3. Dichlorosilane Process/Product Evaluation (3.3)

Acquire kinetic data for liquid phase redistribution of trichlorosilane.

Characterize operating limits, lifetime of catalyst

Analyze purity of redistributed chlorosilanes via silicon CVD.

Acquire safety-related information on dichlorosilane necessary to complete fire/spill protection PDU design.

Order PDU major equipment items.

Initiate PDU construction.

4. Preliminary EPSDU Design (3.4)

Add energy balance data to existing material balance.

Complete Process Flow Diagrams.

6.0 New Technology

No new technology was developed during this quarter.

7.0 References

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3. U. S. Patent No. 2,595,620, assigned to Union Carbide Corp., 1952.
4. Union Carbide Corp., "Final Progress Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 954334, 3/79.
5. See, for example, D. Weyenberg, A. Bey and P. Ellison, J. Organomet. Chem. 3, 489 (1965).
6. Thermodynamic calculations are based on a computer program named "EQUI," developed by L. Hunt of Dow Corning Corp. Thermochemical data have been taken from: L. Hunt and E. Sirtl, J. Electrochem. Soc. 119, 1741 (1972).
7. A. Lekholm, J. Electrochem. Soc. 119, 1122 (1972).
8. J. Burneister, J. Cryst. Growth 11, 131 (1971).
9. Hemlock Semiconductor Corp., "First Quarterly Report", Low-Cost Silicon Solar Array Project, DOE/JPL Contract No. 955533, January, 1980.

8.0 Acknowledgements

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TABLE I. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE
USING TRICHLOROSILANE FEED

<u>RUN NO.</u>	<u>RUN TIME</u> <u>HRS.</u>	<u>ROD</u> <u>DIAMTER</u> <u>MM</u>	<u>SILICON</u> <u>FED</u> <u>gh⁻¹ cm⁻¹</u>	<u>SILICON</u> <u>DEPOSITION</u> <u>gh⁻¹ cm⁻¹</u>	<u>CONV. EFF.</u> <u>MOLE %</u>
394-049-1	27.7	3.0-22.7	1.784	0.334	18.8
394-050-1	28.5	3.0-22.8	1.784	0.328	18.4
394-051-1	9.0	3.5-11.5	1.467	0.244	16.6
394-051-2	11.0	11.5-21.1	4.933	0.521	10.5
394-051-3	8.0	21.1-26.4	3.722	0.576	15.5
394-051-4	6.5	26.4-30.4	3.722	0.640	17.2
394-052-1	32.0	4.5-27.9	3.162	0.434	13.7
394-053-1	5.0	4.5-9.5	1.784	0.256	14.4
394-054-1	31.0	3.5-28.5	3.722	0.473	12.7
394-055-1	7.5	3.5-10.0	1.211	0.214	17.7
394-055-3	12.0	21.5-27.5	1.784	0.448	25.1
394-055-5	6.0	32.0-34.4	1.784	0.486	27.2
394-056-1	27.5	3.5-23.5	1.784	0.359	20.1
394-060-1	27.5	4.5-23.1	1.784	0.342	19.2

TABLE II. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE
USING TRICHLOROSILANE FEED of 1.784 G/HR.

<u>RUN NO.</u>	<u>RUN TIME</u> <u>HRS.</u>	<u>ROD</u> <u>DIAMTER</u> <u>MM</u>	<u>SILICON</u> <u>FED</u> <u>gh⁻¹ cm⁻¹</u>	<u>SILICON</u> <u>DEPOSITION</u> <u>gh⁻¹ cm⁻¹</u>	<u>CONV. EFF.</u> <u>MOLE %</u>
394-049-1	27.7	3.0-22.7	1.784	0.334	18.8
394-050-1	28.5	3.0-22.8	1.784	0.328	18.4
394-053-1	5.0	4.5-9.5	1.784	0.256	14.4
394-055-3	12.0	21.5-27.5	1.784	0.448	25.1
394-055-5	6.0	32.0-34.4	1.784	0.486	27.2
394-056-1	27.5	3.5-23.5	1.784	0.359	20.1
394-060-1	27.5	4.5-23.1	1.784	0.342	19.2

TABLE III. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE USING
DICHLOROSILANE FEED

<u>RUN NO.</u>	<u>RUN TIME</u> <u>HRS.</u>	<u>ROD</u> <u>DIAMETER</u> <u>MM</u>	<u>SILICON</u> <u>FED</u> <u>gh⁻¹ cm⁻¹</u>	<u>SILICON</u> <u>DEPOSITION</u> <u>gh⁻¹ cm⁻¹</u>	<u>CONV. EFF.</u> <u>MOLE %</u>	<u>POWER</u> <u>CONSUMPTION</u> <u>kWh/Kg</u>
394-049-2	8.0	22.7-28.2	1.784	0.641	35.9	190.8
394-050-2	8.0	22.8-32.0	3.412	1.154	33.8	106.7
394-051-5	8.0	30.4-34.7	1.784	0.641	35.9	202.6
394-052-2	8.0	27.9-33.7	1.784	0.817	45.8	159.0
394-052-3	8.0	33.7-37.9	1.784	0.687	38.6	201.3
394-052-4	7.3	37.9-41.5	1.784	0.716	40.2	194.3
394-053-2	6.0	9.5-18.8	3.340	0.802	24.0	94.9
394-054-2	8.0	28.5-36.3	3.340	1.157	34.6	108.7
394-054-3	2.0	36.3-38.4	3.340	1.435	43.0	93.5
394-055-2	8.0	10.0-21.5	3.340	0.828	24.8	89.1
394-055-4	4.0	27.5-31.9	5.094	1.196	23.5	111.5
394-055-6	6.0	34.4-41.6	5.094	1.669	32.8	92.2
394-056-2	4.0	23.5-25.6	1.372	0.471	34.3	128.0
394-056-3	8.0	25.6-35.9	5.094	1.449	28.4	94.6
394-056-4	6.0	35.9-42.3	5.094	1.526	30.0	96.8
394-057-1	3.5	3.5-11.1	3.722	0.579	15.6	94.8
394-057-2	8.0	11.1-18.7	1.784	0.518	29.0	153.2
394-057-3	8.0	18.7-28.9	3.722	1.110	29.8	94.8
394-057-5	5.0	33.4-36.6	1.784	0.820	46.0	155.9
394-058-1	8.0	4.0-16.7	1.784	0.602	33.7	115.2

TABLE IV
QUALITY ANALYSIS DATA FROM SILICON RODS GROWN FROM

- A. Vapor Phase Trichlorosilane Redistribution Products
B. Dichlorosilane (commercial cylinder)

	Resistivity (ohm-cm)	Boron (parts per billion atomic)	Donor
A.	40, n-type	1.0	4.0
B.	3, n-type	1.6	34.3*

* Purity run conducted immediately after disassembly of reactor vent system. This procedure invariably leads to some donor contamination.

TABLE V
DATA FROM STATIC CATALYSIS EXPERIMENTS WITH DOWEX MWA-1
RESIN AND TRICHLOROSILANE

Run Number	:	061	062	073	074*
Catalyst Weight (gms)	:	5	0.5	0.5	None
Reaction Temp (degC)	:	80-85	80-90	84-88	80-81
Reaction Time (mins)	:	180	200	160	160
Reactor Charge (mmoles)	:	21.3	21.5	21.3	19.8
Reactant Mixture					
-mole% TCS	:	100	80	90	100
-mole% STC	:	0	20	10	0
Product Composition					
-mole% MCS	:	0.86	0.3	0.4	0
-mole% DCS	:	12.5	4.6	6.3	0
-mole% TCS	:	72.9	69.1	73.0	100
-mole% STC	:	13.7	26.0	20.2	0
Chlorine Balance					
-In	:	300.0	320.0	310.0	
-Out	:	299.4	320.8	312.8	

* Blank run to insure no extraneous catalytic activity with reaction system components.

TABLE VI. FLOW SCHEDULE FOR EPSDU (FIGURE 11)

Stream	Flow* lb/hr	Mole Fraction						
		H ₂	MCS	DCS	TCS	STC	HCl	Si
AA	509.3	0	0	0	1.0	0	0	0
AB	2990.7	0	0	0	1.0	0	0	0
AC	2990.7	0	0	0	1.0	0	0	0
AD	2990.7	0	0.005	0.105	0.780	0.11	0	0
AE	247.2	0	0	0.23	0.606	0.164	0	0
AF	3238.0	0	0.0046	0.110	0.77	0.114	0	0
AG	288.5	0	0.039	0.922	0.039	0	0	0
AH	2949.5	0	0	0.87	0.13	0	0	0
AI	2481.4	0	0	0	1.0	0	0	0
AJ	468.0	0	0	0	0.01	0.99	0	0
AK	288.5	0	0.039	0.922	0.039	0	0	0
AL		1.0	0	0	0	0	0	0
AM	247.2	X	0	0.202	0.530	0.143	0.126	0 Non Hydrogen Basis
AN		1.0	0	0	0	0	0	0
AO	9.75	0	0	0	0	0	1.0	0
AP		1.0	0	0	0	0	0	0
AQ		1.0	0	0	0	0	0	0
AR	28.08	0	0	0	0	0	0	1.0

* Hydrogen produced in the decomposition reactors is not accounted for in the material balance. The difference of pounds in and out, as shown, is hydrogen.

Time (Mo.)	3	6	9	12	15	18	21	24	27	30	33	36	39
Project													
Phase 1													
DCS Reactor Feasibility													
TCS+DCS Redistri- bution Feasibility													
EPSDU Plant Design													
Intermediate Rx Design and Construction													
Phase 2													
EPSDU Design													
Production Rx. Eval- uation													
Phase 3													
EPSDU Constnution /Demonstration													

FIGURE 1. SCHEDULE OF EFFORTS BY PHASES

BASED POLYCRYSTALLINE SILICON PROCESS

FIGURE 4. PROGRAM PLAN MILESTONE SCHEDULE

FIGURE 4. PROGRAM PLAN MILESTONE SCHEDULE (cont.)

FIGURE 5
POLYCRYSTALLINE SILICON ROD
GROWN DURING RUN 394-056

FIGURE 6. CHROMATOGRAPHIC DATA FROM RUN 394-057-5

CODS

(R) Regulator	(N) Needle Valve	Check Valve	Solenoid Valve
(BR) Back Pressure Regulator	(C) Flow Controller	1/4" Ball Valve	Safety Relief
(P) Pressure Gauge	(W) Glass Window	Filter	Rotameter

FIGURE 7. SCHEMATIC OF LABORATORY TRICHLOROSILANE REARRANGER UNIT

FIGURE 8.
LABORATORY REARRANGER UNIT

OIL BATH FOR
CATALYST COLUMNS

FIGURE 9. GAS CHROMATOGRAPHIC TRACE OF REDISTRIBUTED
CHLOROSILANES FROM LABORATORY REARRANGER
UNIT EXPERIMENT

FIGURE 10. SCHEMATIC OF DICHLOROSILANE MINI-PLANT

FIGURE 11. MAJOR MATERIAL FLOWS IN EPSDU