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DOE/JPL/955533-79/1

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

First Quarterly Progress Report for October 6—December 31, 1979

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January 1980

Work Performed Under Contract No. NAS-7-100-955533

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U.S. Department of Energy

Solar Energy

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FIRST QUARTERLY PROGRESS REPORT

6 October to 31 December 1979

on

DEVELOPMENT OF A POLYSILICON PROCESS
BASED ON CHEMICAL VAPOR DEPOSITION

(PHASE 1)

prepared by

MASTER

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and

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January 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."

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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.

Chemical processes involved in achieving the above objective are reviewed with emphasis placed on advantages of this process when compared with existing polycrystalline silicon production technology.

Installation of a CVD reactor with associated analytical instrumentation is described. Preliminary reactor data has been favorable demonstrating the anticipated increased deposition rate and conversion efficiency when dichlorosilane decomposition is compared with trichlorosilane decomposition. No serious problems have been encountered which might limit dichlorosilane use as a reactor feed material.

Design considerations for a process development unit (PDU) for dichlorosilane synthesis are reviewed. A design which effectively suppresses monochlorosilane during the redistribution of trichlorosilane was decided upon and its implementation is described. The PDU will be used to collect data on optimization of the redistribution process as well as to determine product quality.

Based on experimental data collected during the first quarter along with already available data on the redistribution and hydrogenation processes, a preliminary mass balance is established.

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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 recycled 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 a 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 EPSDU level.

The chemistry relevant to this process is reviewed and advantages of this process over the existing Siemens polycrystalline silicon production process are discussed.

An experimental CVD reactor system designed for use with dichlorosilane feed and associated analytical instrumentation was placed in operation. In the limited number of CVD runs completed in the first quarter results, have been encouraging. Silicon deposition rates obtained using dichlorosilane feed are significantly greater than those observed using trichlorosilane under comparable reactor operating conditions. No problems unique to the use of dichlorosilane as a reactor feed material have been encountered. With the exception of some unreacted dichlorosilane present in the decomposition byproduct stream, vent gas composition contains those chlorosilane species observed in trichlorosilane decomposition.

A PDU (mini-plant) was designed to provide sufficient dichlorosilane for extended reactor operation and evaluate the quality of dichlorosilane produced via the redistribution of trichlorosilane. A mixed feed (HSiCl_3 - SiCl_4) redistribution process coupled with a single distillation

step is described. This process was determined to be the most cost effective approach to pure dichlorosilane preparation.

Laboratory equipment was installed to support PDU efforts. Evaluation of Dowex Resin MWA-1 as a redistribution catalyst was initiated. Dowex Resin MWA-1 decomposition characteristics including loss of functional amine is under investigation.

A preliminary material balance is presented encompassing hydrogenation, redistribution and reductive chemical vapor deposition. Experimental data obtained at HSC as well as data available in the literature relating to the hydrogenation process was used in establishing this material balance.

The quality of the silicon produced to date is comparable to that produced via Siemens technology. In the first three months of this project, we have demonstrated that silicon can be deposited from dichlorosilane at rates which substantially exceed those possible with trichlorosilane under comparable conditions.

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 in high volume a low cost polycrystalline silicon. 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 DCS Reactor Development)
3. Design, construction and operation of a process development unit to characterize the trichlorosilane to dichlorosilane redistribution process, determine product purity, and produce sufficient dichlorosilane to permit operation of a production sized reactor. (DCS Process/Product Evaluation)
4. Conduct preliminary design of an 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 along with a discussion

of relevant chemistry . 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

Chemical vapor deposition (CVD) of high purity polycrystalline silicon from a chlorosilane feedstock forms the basis of the entire semiconductor-grade polycrystalline silicon industry. These processes, utilizing trichlorosilane as an intermediate material, (feedstock for CVD) currently produces material of proven quality to meet the demanding needs of the electronics industry as well as the emerging photovoltaic industry. Current worldwide capacity is approximately 2,500 metric tons with capacity divided among a number of producers.¹ Process improvements coupled with expanding capacity have resulted in a steadily declining polycrystalline silicon price in terms of constant dollars. The industry has established a technology base sufficient to permit rapid commercialization of a chlorosilane based process. The inability of the current polycrystalline silicon process to meet the goals of the DOE/JPL program is a matter of high manufacturing costs-not product quality or raw materials availability.

The current process employed in polycrystalline silicon production is shown schematically in Figure 2. It consists of the hydrochlorination of metallurgical-grade silicon to produce trichlorosilane; distillation of this material to achieve adequate product purity; reductive chemical vapor deposition to produce high purity polycrystalline silicon, and by-product recovery. Weaknesses in the process which contribute to high product cost, as compared to the \$14/kg JPL goal*, may be readily identified by considering previous economic evaluations of the process!¹⁰ These shortcomings can be summarized as follows:

* Cost figures are expressed in 1980 dollars

1. High unit capital cost of CVD reactors due to low deposition rate.
2. High power consumption of the CVD process.
3. Production of substantial amounts of the byproduct silicon tetrachloride.
4. Relatively large CVD reaction byproduct stream requiring a sizable recovery system.
5. Thermodynamic limitation on conversion (into silicon) efficiency.

Considering these shortcomings along with the maturity of the current process and the ability of its product to meet requirements for high efficiency cell manufacture, innovations which could significantly reduce product cost were evaluated. The resulting low cost process for the production of high quality polycrystalline silicon via reductive chemical vapor deposition from dichlorosilane is depicted in Figure 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 byproduct of trichlorosilane redistribution and minor byproduct of dichlorosilane decomposition is recycled into the hydrogenation process. Also shown in Figure 2 are the distillation processes required for chlorosilane separation/purification.

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

This process addresses the shortcomings of the current trichlorosilane process by:

1. Use of dichlorosilane as a feed material for the CVD process. Dichlorosilane decomposes more readily than trichlorosilane, resulting in higher deposition

rates.^{2,3,4} This leads to reduce labor and capital costs. Dichlorosilane also produces less vent material, thereby reducing capital associated with the recovery system.

2. Hydrogenation of SiCl_4 to produce trichlorosilane. This process accomodates 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 under other JPL contracts by Union Carbide Corporation indicate that the hydrogenation process can produce trichlorosilane cost-effectively.^{5,6}
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, with its years of experience in reductive chemical vapor deposition using trichlorosialne 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 polysilicon via the decomposition of dichlorosilane include:

Hydrogenation of Silicon Tetrachloride

Dichlorosilane Synthesis

Catalyst

Dichlorosilane Decomposition

The above equations are written only qualitatively since exact reactor products are temperature- and composition-sensitive. Relevant points regarding the advantages and limitation of these reactions are now discussed.

HYDROGENATION OF SILICON TETRACHLORIDE

The substantial amount of silicon tetrachloride which is generated in the redistribution and decomposition process 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.⁶ Although the yield of hydrogenation is expected to be <30%, the only byproducts are unreacted hydrogen and silicon tetrachloride, which are recycled. UCC is currently funded for demonstrating technology readiness of the hydrogenation process as part of their low cost silane effort. 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 Corning,⁷ UCC⁶ and elsewhere has demonstrated the preferred route to dichlorosilane to be the acid or base-catalyzed redistribution of trichlorosilane.

This process is superior to a "direct process" reaction of HCl with silicon. Such a direct reaction invariably generates considerably more trichlorosilane than dichlorosilane. 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, non-volatile 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 UCC have demonstrated that an amine-functionalized 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. The resin is a methyl amine-modified organic polymer supplied as spherical beads averaging 0.4 mm in diameter. It is supplied as a water-saturated material and must be thoroughly dried prior to use.

Equilibrium relationships among chlorosilanes are known from research conducted at both Dow Corning⁷ and Union Carbide.⁶ 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. Because of safety and handling considerations, it is desirable in the PDU stage and may be desirable in the commercial process to feed a mixture of Cl/H greater than 3 to the rearranger to suppress formation of monochlorosilane. An 80/20 mixture of trichlorosilane/silicon tetrachloride should accomplish this purpose, albeit at the expense of lower conversion to dichlorosilane.

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 % chlorosilane (in H₂) as a reactant, the equilibrium conversions of trichlorosilane and dichlorosilane into silicon are, respectively, 40% and 65%.²

A perspective on equilibrium relationships between the two chlorosilanes is presented in Figure 4. The figure shows the Cl/H ratio in the reactor feed stream (and vent, since no hydrogen or chlorine is deposited in the reactor) versus the equilibrium-determined Si/Cl ratio in the vent products (that is, not including the elemental silicon deposited). The figure can be used to ascertain the % conversion into silicon for a range of feed compositions (Cl/H ratios), since

$$\% \text{ conversion} = \frac{(\text{Si/Cl}) \text{ in} - (\text{Si/Cl}) \text{ out}}{(\text{Si/Cl}) \text{ in}}$$

At a feed of 10% dichlorosilane in H₂ and 1050° C, for example, the Cl/H ratio = .10, and:

$$\text{conversion} = (.50 - .20) / .50 = 60\%$$

A further thermodynamic advantage of dichlorosilane relative to trichlorosilane is its lower sensitivity to increases in reactant concentration. For trichlorosilane, doubling the mole % of reactant from 7 to 14% decreases the percent conversion into silicon from 40 to 31 %. Dichlorosilane suffers proportionately less from concentration increases; an increase from 7 to 14% causes an equilibrium conversion decrease from 65 to only 58%.

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 the 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. Typical values are 13 and 22 kcal/mole,^{8,9} respectively. Conditions utilized in epitaxial reactors typically involve substantially lower mole % chlorosilane and flow rates than polysilicon production process reactions. However, recent work by Ban of RCA Laboratories³ has been conducted at mole fractions and temperatures compatible with the polycrystalline silicon production process. Ban's work can be summarized in Figure 5. in which decomposition rates for dichlorosilane, trichlorosilane and silicon tetrachloride are plotted vs. temperature. It is evident from the figure that under conditions in which silicon tetrachloride and trichlorosilane are far from equilibrium conditions, dichlorosilane has achieved or surpassed (1) equilibrium. Yields in excess of equilibrium values may be related to inaccuracies of system analysis or, as Ban suspects, non-equilibration of HCl with the elemental silicon in the system. Ban's work, along with other recent related work indicates that the activation energy for decomposition of dichlorosilane into silicon is considerably less than that for trichlorosilane under a wide variety of conditions.

Additional support for closer approach to equilibrium in dichlorosilane systems comes from Union Carbide patents which claim conversions into silicon of up to 60% in a single rod CVD reactor.⁴

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 as previously discussed

generates substantial quantities of silicon tetrachloride; with dichlorosilane as a feed material, the principal by-products should be a mixture of trichlorosilane and unreacted dichlorosilane. This assumption has been borne out in preliminary gas chromatographic analyses of runs on an experimental reactor.

These by-products (trichlorosilane, silicon tetrachloride, HCl and unreacted dichlorosilane) of the reaction which generates silicon from dichlorosilane are an important part of the chemical scheme. The expense of operation of the recovery system, which must separate the components, and the amount of silicon tetrachloride generated, which would have to be sold or recycled in a separate process are obviously dependent on the specific product distribution.

Unfortunately, equilibrium calculations cannot provide unambiguous values for vent gas composition: mass balance requirements can be met with a variety of combinations of individual concentrations. For example, Figure 6 shows possible combinations of trichlorosilane, silicon tetrachloride and HCl concentrations for an assumed percent conversion to silicon and % unreacted dichlorosilane.

2.3.2 Process Implementation

Implementation of the low cost chlorosilane based CVD process is illustrated schematically in Figure 7. Hydrogenation of silicon tetrachloride occurs in a fluidized bed reactor. The fluidized bed is made up of finely ground metallurgical grade silicon fluidized with 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 chlorosilanes 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. A general discussion of the basic processes contained in the recovery system appears in reference 1.

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, it 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 their efforts 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 8. These four major areas of technical activity are discussed Sections 3.1 through 3.4.

3.1 CVD Reactor Feasibility

3.1.1 General

The objectives of the reactor feasibility task are:

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 a 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 EPSDU 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 and Support System

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 dichlorosilane conversion and vent product composition required for EPSDU design.

A schematic of reactor 394 showing feed and vent line configuration is shown in Figure 9. This arrangement allows various combinations of feed (trichlorosilane, dichlorosilane, or rearranged material) to be supplied to the reactor. This configuration permits dichlorosilane and trichlorosilane feeds to be mixed in any proportion at the reactor inlet manifold. Rotameters are used to measure flow rate, and Hoke needle valves to control flow rate through the rotameters.

The vapor phase rearranger can be operated independently or in conjunction with reactor 394. Figure 10 is a schematic of the rearranger piping. The stream leaving the rearranger can be monitored by the gas chromatograph (GLC) for any desired mode of operation.

The rearranger is constructed of 2" O.D. carbon steel pipe, with a flange at the top to allow packing and unpacking of Dowex MWA-1 catalyst, and with distribution plates at both ends. The unit is 24 inches in length and has type K thermocouples located in thermowells at the top and bottom heads. The unit is electrically heat traced and insulated.

The rearranger has been preconditioned by outgassing at operating temperature (50-85°C) under high vacuum. It was then precharged with trichlorosilane overnight at operating temperature. The rearranger has been designed for a maximum 30% trichlorosilane gas flow of 45 SCFH at 30 psig pressure.

Since the rearranger will need periodic service a nitrogen purge manifold is connected to the inlet of the unit.

Electronic grade dichlorosilane feedstock for 394 reactor is purchased from Union Carbide Corporation in 50 pound or 250 pound steel cylinders. The cylinders are equipped with a two-stage regulator specifically designed for dichlorosilane. A nitrogen purge manifold is connected between the cylinder and regulator. A schematic of the dichlorosilane cylinder piping is presented in Figure 11.

Cylinders must be heated to vaporize dichlorosilane in sufficient amounts to operate the CVD reactor. Heat is provided by means of electrical heating tape. A temperature of approximately 46°C produces a cylinder pressure of 40 psig. The heat tape is a current-limiting type with a maximum attainable temperature of 76°C, well below the autoignition temperature of dichlorosilane. The cylinder skin temperature is monitored with a thermocouple. A pressure switch at the cylinder outlet is used to control power to the heating tape. If the cylinder pressure exceeds a preset value of 50 psig power is automatically shut off.

Stainless steel tubing (3/8" diameter) is connected from the cylinder to the inlet manifold of 394 reactor. This feed line is wrapped with electrical heating tape and insulated to prevent condensation of dichlorosilane.

After the feed material is mixed with hydrogen at the manifold, it is introduced into the reactor. The reactor is composed of four parts, consisting of a heat shield, quartz bell jar, baseplate, and power supply.

The heat shield protects operating personnel from the intense heat of the reactor which radiates through the quartz bell jar. It also contains reaction products should the bell jar crack during operation. The quartz bell jar is a containment vessel 12 inches in diameter, 24 inches in height.

The baseplate is water cooled and is equipped with various sight ports which allow viewing the silicon and obtaining temperature measurements. Feed material enters the reactor through a nozzle located in the center of the baseplate, and vent products exit through a hole in the baseplate which is slightly off-center. The baseplate has four electrodes. Three-millimeter diameter cylindrical substrate rods are tightly fit into the electrode chucks. The power supply must be capable of delivering a wide range of voltages and amperages to produce resistive heating of the substrate.

Key parameters relating to CVD reactor silicon production such as silicon deposition rate, composition of the vent gas, and available surface area for reaction, are time-dependent. In order to ascertain "instantaneous" rather than run-averaged values for such parameters, a real-time analytical system has been installed in support of reactor research and development. A system developed for internal research efforts is being used on an interim basis to support the research described in this report; a similar system will be implemented as soon as possible and utilized entirely for dichlorosilane optimization efforts.

Both systems consist of three major subsystems: a Bendix process gas chromatograph, a Perkin-Elmer Sigma 10 data system, and a North Star Horizon microcomputer. The three subsystems and their interconnections are shown in Figure 12.

The process gas chromatograph is a Bendix model 170, configured for isothermal column operation and thermal conductivity detection, and is located in proximity to the research reactor. It is connected to both the feed and vent lines of the experimental 12 inch reactor being used in this project. Operation of chromatographic events such as valve switching, and processing of the analog detector signal from the chromatograph is handled by the Sigma 10 data system located in another room in the reactor building.

The Sigma 10 consists of a digitizing integrator, instrument controller, data processor and printer/plotter all in a compact table top unit. Chromatographic "methods" written by the user specify the sequence of events of chromatograph operation, and the details of data reduction, output and storage by the Sigma 10.

After the raw chromatographic data are partially processed by the Sigma 10, they are stored on microcassettes. At a later time, these data are transmitted via a dedicated phone line to the third component, a Horizon microcomputer. The Horizon is capable of much more powerful data reduction and mass storage on floppy disks. It is connected to a number of peripherals, including the digital plotter. Basic programs have been written for the Horizon which permit raw peak area chromatographic data to be transformed in to mole percent or weight percent vent concentrations, and by comparing adjacent feed and vent samples, into "instantaneous" values for silicon deposition rate and percent conversion. Detailed knowledge of behavior of time-dependent parameters during a reactor run is therefore accessible by means of this analytical system. Details of the chromatographic data provided by this system are discussed in Section 3.1.3.

3.1.3 Experimental Results

In order to provide comparisons of CVD characteristics of dichlorosilane with well understood characteristics of trichlorosilane, baseline trichlorosilane experiments are being conducted to characterize 394 reactor and validate scale-up projections to production reactors.

Operating limits for dichlorosilane are being investigated over a wide range of reactor conditions. Once these limits are established, an experimental design program will provide the necessary information for scale-up to an intermediate size dichlorosilane reactor.

As the decomposition reaction proceeds throughout a run, conditions inside the reactor change. In particular, bell jar operating temperature increases to the point that silicon deposition may take place on the bell jar inner surface. The adherence of the silicon can damage the bell jar due to the different expansion coefficients of quartz and silicon. In addition, this silicon can become detached from the bell jar and degrade silicon surface quality, cover sight parts, or bridge an electrode to the baseplate.

Silicon rods can be grown to 40-45 mm diameter with trichlorosilane feed in reactor 394. For this reason the decomposition of dichlorosilane will be limited to substrates of less than 45 mm in diameter.

To conserve time and dichlorosilane, experimental runs in reactor 394 are being segmented. Trichlorosilane is being used in earlier segments of runs, while dichlorosilane is being used in later segments where reactor operating conditions are more severe. Once a segment is terminated, the bell jar is removed and the polycrystalline silicon rods are measured. Silicon deposition on the bell jar and polysilicon rod quality are noted, and baseplate deposits observed. The bell jar is then replaced, the polysilicon rods are refired, and another deposition segment is carried out. No problems have been encountered using this procedure.

Table 1 summarizes results of using trichlorosilane as feedstock to reactor 394. An example of how a run is segmented can be observed from run number 394-051. Rod diameter measurements were taken at the end of each segment. This data was used to determine the amount of silicon deposited, and from this information the conversion efficiency (grams of silicon deposited per hour /grams of silicon fed per hour) was calculated.

Table 2 summarizes results of reactor performance using dichlorosilane as feedstock. These experiments are the continuation of the trichlorosilane runs represented in Table 1.

Rod diameter measurements and conversion efficiencies are calculated in the same manner as those for trichlorosilanes.

As the deposition reaction progresses, the polysilicon rods increase in diameter. In general, for a fixed trichlorosilane feed rate the conversion efficiency climbs to a peak value and then levels off. Conversion efficiency increases because more reactive sites are available as polysilicon rod surface area increases. The conversion efficiency levels off after the reactor comes to an operational steady state. An example of this phenomenon can be found in Table 1 by comparing runs 394-053-1 with 394-049-1 and 394-050-1. These are typical results using trichlorosilane in a small experimental C-reactor.

Segments 3 and 4 of run 394-051 have yielded the highest deposition rates achieved to date with trichlorosilane. For rod diameters in the 20.0 mm to 30.5 mm range, deposition rates of 0.615 and 0.624 g-Si-h¹-cm⁻¹ were achieved for a silicon feed rate of 672 g-Si-h⁻¹ with a resultant conversion efficiency of 15.3 and 15.6 percent respectively.

Run number 394-044 reported in Table 2 was one of the early attempts to feed dichlorosilane to the reactor. This experiment was conducted prior to the start of JPL contract 955533. Conversion efficiency and silicon deposition rate were the highest ever encountered in this experimental reactor for 322 g-h¹ silicon fed. Operational problems were minimal at these feed conditions, and silicon deposit on the bell jar was no different than any comparable trichlorosilane run.

Since dichlorosilane feed did not pose a problem during the first part of a run, run number 394-049-2 was made to see if problems existed during an intermediate segment at (22mm 28mm diameter) at the same feed conditions. Conversion increased slightly (increasing rod surface area), but results were similar to the earlier run (394-044).

The dichlorosilane feed rate was nearly doubled for run number 394-050-2 to determine what operational problems existed at these conditions. This produced the highest

deposition rate (1.175) to date with little sacrifice of conversion (32.0%). Silicon deposition on the bell jar was thin ($<1/64$ " thick) and was typical of a trichlorosilane run under comparable conditions. The only operational problem encountered was inadequate dichlorosilane cylinder pressure during the entire run. Consequently, the run was interrupted periodically to bring the cylinder pressure up to its operating range.

Run 349-051-5 was made to verify earlier results obtained from 349-049-2 and to use the last portion of dichlorosilane from the cylinder at the lower feed rate, as well as to produce more data at a larger rod diameter. As the run progressed the cylinder pressure dropped continuously, which resulted in a lower conversion efficiency and reduced deposition rate. Silicon deposition on the bell jar occurred only in the dome area.

Run 394-052 was a segmented dichlorosilane experiment. Improved temperature control on the dichlorosilane cylinder significantly improved reactor operation. Run 394-052 has produced the largest diameter material and highest conversion efficiencies to date. Segments 2 and 3 had a thin silicon deposit in the dome of the bell jar. Segment 4 had a very thin layer of silicon over the entire inner bell jar surface. This behavior is comparable to trichlorosilane at the same feed conditions and rod diameter.

When the data presented in Table 1 and Table 2, are compared the most noticeable result is that no matter what diameter polysilicon rod or feed rate, dichlorosilane is far superior to trichlorosilane as a vehicle for CVD deposition of silicon. Conversion efficiency of dichlorosilane and deposition rate are twice that of trichlorosilane at similar feed rates, all other reactor conditions being constant. In addition, operational problems have been minimal.

Chromatographic data derived from two reactor runs are represented in Figures 13 and 14. The runs were conducted with the same flow and composition of feed. In each of the runs, feed and vent lines are sampled alternately, with a

frequency usually in the range of 4-5 per hour. Five components--HCl, SiH_3Cl , SiH_2Cl_2 , SiHCl_3 and SiCl_4 -- are routinely monitored.

The figures indicate time-dependence of relative molar concentrations for reactor vent samples taken during runs 394-044 and 394-052-2, respectively. Run 394-044 was made with the 3 mm "slim rods" normally present at the beginning of a run. Dichlorosilane was fed to the reactor for 8 hours, at which time the run was terminated. The chromatographic data indicate a substantial change in the concentration of two of the components, (H_2SiCl_2 and HSiCl_3) and a smaller change in the other two components during the run.

Dichlorosilane is initially by far the most abundant component of the vent stream. However, as the run progress, the dichlorosilane concentration falls appreciably, while that of trichlorosilane increases. The two curves cross after approximately 5 hours. During the entire 8 hour run, HCl concentration increases only slightly, while silicon tetrachloride exhibits a slow but steady increase from its very low initial concentration. It is apparent from the figure that steady state reactor conditions have not been attained.

In contrast to run 394-044, run 394-052-2 was conducted with 30 mm diameter silicon rods (grown with trichlorosilane) present at the outset. This approach should simulate the "mature" portion of a run in which both vent composition and deposition rate have stabilized. This is borne out by the data shown in Figure 14. Except for a slight concentration increase for silicon tetrachloride and slight decrease for dichlorosilane, the concentrations are remarkably constant. Comparison with the previous figure substantiates the trends observed in the small rod run: dichlorosilane is now the lowest in concentration among the four major components, and silicon tetrachloride has crept ahead of HCl. Trichlorosilane is about where one would predict from extrapolation of the curve in Figure 13.

3.2 Intermediate Dichlorosilane Reactor Development

3.2.1 General

Scale-up projections based on performance of reactor 394 will be verified using an intermediate size reactor. Operational requirements of this reactor will be defined to insure that reactor performance will be indicative of that of production reactors designed for the EPSDU. Once reactor requirements are established, a reactor and dichlorosilane feed system will be designed to permit feeding the reactor material produced from the dichlorosilane PDU.

Crucial reactor parameters have been identified for consideration in intermediate reactor design as well as EPSDU design. Parameters under analysis include: bell jar volume, bell jar height, bell jar diameter, deposition substrate length, deposition substrate diameter, voltage required, current required, chlorosilane and hydrogen flow rates, and vent gas composition and temperatures. Although the analysis is in the very early stages, it appears that a modification of an existing HSC production reactor may be adequate to demonstrate intermediate DCS reactor performance.

Detailed analysis of reactor requirements will be completed in the second 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

The PDU support effort is designed to provide data in four general areas

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

Requirements for and status of work in each of these areas are covered below.

PROCESS STREAM ANALYSIS

In order to monitor and control the PDU process some form of liquid product stream analysis is desirable. The simple method is gas chromatography (GLC). Besides the basic GLC equipment, information on the detector response factors for the various chlorosilanes, i.e. in particular dichlorosilane and monochlorosilane, and a method of sampling the pressurized liquid process chlorosilane streams are required. The approach to the former is to prepare calibrated mixtures of the chlorosilanes via conventional vacuum techniques, inject these into the gas chromatograph and compare peak areas relative to trichlorosilane to obtain the necessary detector response factors.

The approach to GLC sampling techniques will be to determine the feasibility of the following techniques and select the most reliable and efficient.

- Direct syringe injection of the liquid chlorosilanes into the GLC
- Injection of the liquid chlorosilanes into the GLC via an automatic liquid sampling valve
- Flash evaporation of the liquid chlorosilane and subsequent gas injection into the GLC

A Varian Model 3400 gas chromatograph with automatic injection valve and associated accessories and supplied has been ordered. This chromatograph will be dedicated to the DCS Intermediates process in both the laboratory and PDU programs. This unit will arrive and be operational during the first quarter of 1980.

All other equipment has been set up and procedures developed for preparing calibrated mixtures of chlorosilanes for use in determining detector response factors for dichlorosilane and monochlorosilane. Equipment and procedures already exist for trichlorosilane and silicon tetrachloride.

CATALYST STABILITY

Since the solid catalyst used to effect the redistribution of trichlorosilane, i.e., Dowex Ion Exchange Resin MWA-1, is an organic amino functional material, its thermal stability is of concern. Of particular importance is the extent to which it loses nitrogen at elevated temperatures and whether this nitrogen is in a reactive and volatile form such as a methyl amine. Such a material might cause problems in the distillation and storage of dichlorosilane, i.e., redistribution to monochlorosilane and silane.

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

The following properties of Dowex ion exchange resin have been determined experimentally since the program was initiated:

Moisture Content	50-52 wt%
Bulk Density	0.54 gms/cc (wet) 0.35 gms/cc (dry)
Deformation (and Particle Bridging)	None @ 189° C and 0 psi load (after 28 hours) None @ 129° C and 32 psi load (after 4 hours)

Bed Swelling (Dry to Wet) 22% in Acetone

12% in Silicon Tetrachloride

Various methods for drying the resin catalyst were evaluated during the first quarter, including: solvent displacement vacuum drying, oven drying, dessication and inert gas purging. With the exception of dessication, all of these methods were equally effective in removing the moisture. The data are presented in Table 3. The evolution of hydrogen chloride gas when the "dried" samples were placed in silicon tetrachloride was used as a measure of the effectiveness of the drying procedure. Inert gas purging with dry argon (or nitrogen) followed by preconditioning with liquid silicon tetrachloride appears to be the most practical from a production standpoint. Static electrical charge build-up on the surface of both wet and dry Dowex resin make handling of the bulk material somewhat difficult. This static electrical charge appears to be effectively dissipated when the material is immersed in polar liquids such as acetone or silicon tetrachloride but remains when the resin is immersed in hexane.

A sample of dry Dowex resin was heated at increasing temperatures and the decomposition products at each temperature collected and measured by conventional vacuum line techniques. The type of decomposition materials was subsequently determined by gas phase infrared analysis. The data from these experiments are presented in Table 4. It should be noted in Table 4 that substantial decomposition occurs at $>150^{\circ}\text{C}$ but that once the resin is "baked out," subsequent decomposition is greatly retarded (note the decomposition percent from run C-054 which followed C-050). The decomposition product, trimethylamine, is of concern since this is an active catalytic species which can promote further redistribution of the product dichlorosilane to monochlorosilane either in the catalytic reactor, the distillation unit or in product storage. It is not known at this time whether the amount of trimethylamine evolved is sufficient to cause an operational or safety problem.

A second series of experiments was performed in which a sample of Dowex resin was heated in a vacuum drying oven and the weight loss of the sample determined at successively higher temperatures. The data are presented in Table 5. Again it may be noted that extensive decomposition occurs at $>147^{\circ}\text{C}$, a temperature high above that which operation of the redistribution column is anticipated.

REDISTRIBUTION KINETICS

According to the chemical principles previously described, it appears practical 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 will be 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 obtain information on product purity by depositing silicon from the material produced by this laboratory unit.

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

All parts have been ordered and initial construction is underway. This unit should be constructed, safety audited and started up during the first quarter of 1980.

PRODUCT AND PRODUCT STREAM SAFETY

Although some data are available concerning the hazards and precautions for silicon tetrachloride, trichlorosilane, dichlorosilane and silane, little is known about monochlorosilane. There is concern that small amounts of monochlorosilane (and silane) formed via direct redistribution (or in storage if catalytically active decomposition products of Dowex resin are present) may be a distinct and perhaps substantial safety hazard. Although much can be safely learned 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.

As noted in the section on "Catalyst Stability", Dowex resin evolves trimethylamine on heating. Since this is an active catalytic species which could cause subsequent undesirable redistribution of dichlorosilane to monochlorosilane and silane, a potential safety problem may exist. The magnitude of this problem, if one does exist, is not known at this time. It appears from the data that the evolution of trimethylamine is reduced by "baking out" the resin at a temperature higher than the planned use temperature.

The Materials Safety Data Sheets (OSHA Form 20) are being collected and assembled on all the materials involved in the DCS Intermediates process, i.e., dichlorosilane, trichlorosilane, silicon tetrachloride, silane, Dowex ion exchange resin, hydrogen chloride, hydrogen, chlorine, argon, nitrogen and helium. Assembly should be completed during the first quarter of 1980.

A program will should be implemented during the first quarter of 1980 in cooperation with Dow Corning Corporate Safety personnel to define what information is needed and

what work must be done to assess the safety hazards associated with monochlorosilane and dichlorosilane.

3.3.3 Process Development Unit Design

The process development unit, PDU, is designed to produce and purify dichlorosilane to meet Phase 1 objectives. Major components in the PDU are the rearranger (redistribution reactor) and the distillation column for chlorosilane separation. The rearranger converts trichlorosilane to dichlorosilane and silicon tetrachloride in the presence of an amine-functional catalyst. Dichlorosilane is then purified by the distillation column to >99 mole percent in a continuous operation. PDU sizing was established at a rate of 35 lb/hr. compatible with a 2000 lb/wk. production schedule. This rate allows a three day per week operation to provide sufficient dichlorosilane to operate one production scale decomposition reactor. The three day schedule allows two technicians to operate the equipment on twelve hour shifts. Higher production rates result in excessive initial equipment procurement costs.

The redistribution/distillation unit should provide a product which consists of 99 mole % dichlorosilane, 1 mole % trichlorosilane, and a small amount of monochlorosilane. This will permit accurate evaluation of dichlorosilane in the decomposition reactor, while avoiding potential safety and operational problems with monochlorosilane.

The product specification to have only small quantities of monochlorosilane in the dichlorosilane requires a design either to prevent formation of or separation and disposal of monochlorosilane. Figures 16 and 17 depict designs incorporating these two schemes.

The single still system shown in Figure 16 includes two feed tanks, a feed heater, a redistribution reactor, a distillation column and a product storage tank. In operation the feed tanks would be used alternately for storage of feed material and still bottoms product. The feed material would

be blended to a desired trichlorosilane/silicon tetrachloride composition. Feed is preheated prior to entering the redistribution reactor. The reactor effluent flows directly to the distillation column. Here the dichlorosilane and any trace low boiling materials are separated and removed as overhead product. The overhead product is stored until required as feed to the decomposition reactor. The still bottoms material is sent to the other feed tank where it will later be mixed with more trichlorosilane and fed to the redistribution reactor.

The three-still system shown in Figure 15 would feed pure trichlorosilane through a feed heater, then to a redistribution reactor. The reactor effluent in this case would contain approximately 7 mole % as much monochlorosilane as dichlorosilane. The monochlorosilane and dichlorosilane would be removed as overhead product from the first column and the trichlorosilane and silicon tetrachloride would be contained in the first still bottoms. Still 2 would separate trichlorosilane from the silicon tetrachloride for recycle. Still 3 would separate monochlorosilane from dichlorosilane. The dichlorosilane would be stored until needed for silicon production. The monochlorosilane would be blended with silicon tetrachloride to provide a suitable chlorine/ hydrogen ratio to permit recycle to the redistribution reactor.

The single still arrangement of Figure 16, with monochlorosilane suppression, although requiring a larger distillation column and redistribution reactor, will cost significantly less than the three still system which accommodates monochlorosilane separation and disposal. This fact is due to the more complex instrumentation as well as the additional equipment and piping needed to construct and operate three distillation columns as opposed to one.

Based on the above considerations Figure 18 shows the preferred PDU design. Normal operation is anticipated to proceed as follows. A specified mixture of trichlorosilane and silicon tetrachloride will be added to tank A. Valving will be aligned to allow flow from tank A to the pump.

Valving will be aligned to allow flow from the still bottoms to tank B. The pump will be started and operated with total recycle from discharge to suction and flow through the feed heater. When the operating temperature is established, flow will be established through rearranger E, with rearranger effluent going directly to the distillation column.

Distillation column G will separate the dichlorosilane from trichlorosilane and silicon tetrachloride. The overhead condenser, H, provides liquid for use as reflux or product take off, which is stored in tank J. Just prior to tank A running dry, the material in tank B will be sampled and sufficient trichlorosilane will then be added to the tank to attain the desired feed concentration for the rearranger. Valving will be altered so that tank B supplies feed and tank A receives still bottoms products.

At the end of a run, either tank A or B will be nearly full of a trichlorosilane/silicon tetrachloride mixture that is rich in silicon tetrachloride. Silicon tetrachloride will then be removed from the mixture by distillation in the same column previously used to purify the dichlorosilane. It will be returned to the Hemlock Semiconductor Plant system. A trichlorosilane/silicon tetrachloride mixture at the desired rearranger feed concentration will be returned to the other tank for reuse in a subsequent dichlorosilane production run.

Site selection has been narrowed to two locations at Hemlock Semiconductor. These are referred to as S-22 and S-S-25. Finalization of site selection requires an economic review after consideration of codes, insurance requirements, and needs for added spill protection, added structural steel, and additional foundations.

3.4 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 separate JPL contract.

3.4.2 Status

A very preliminary mass balance has been completed for the entire low cost dichlorosilane process. Figure 10 summarizes the molar material balance for the entire process for the production of 100 moles of high purity polysilicon. Recycle contributions to the material balance are shown in parentheses. The production of 100 moles of silicon requires the introduction of a net 94 moles of metallurgical grade silicon and 6 moles of silicon tetrachloride. The chlorine is lost to the process as HCl produced in the decomposition process. This analysis excludes material loss in process waste streams used for impurity reduction. As in the case of the UCC silane process, this process is characterized by large silicon tetrachloride and trichlorosilane recycle streams. These estimates will be refined as additional data are generated in the course of the program.

4.0 Conclusions and Recommendations

Dichlorosilane decomposition characteristics do not appear to pose a serious problem to its use as a feed material for a reductive chemical vapor deposition process. As anticipated silicon deposition rates achieved using dichlorosilane feed have been significantly greater than those observed when trichlorosilane is fed to a reactor under similar operating conditions. Conversion efficiency for dichlorosilane is approximately twice that observed with trichlorosilane.

A relatively simple redistribution-distillation system employing a single distillation column for the synthesis of pure dichlorosilane via a base catalyzed redistribution of trichlorosilane represents the most cost effective approach for producing material required to demonstrate overall process feasibility.

The program is proceeding on schedule. Preliminary CVD reactor data is highly encouraging and it is recommended that the program proceed according to schedule for the next quarter.

5.0 Program Schedule/Plans

The program is proceeding according to plan. Efforts planned in the various task areas in accordance with the Program Schedule shown in Figure 8 are summarized below.

1. Reactor Feasibility (3.1)

- Complete evaluation of dichlorosilane decomposition characteristics within operating limits of Reactor 394.
- Optimize decomposition conditions in Reactor 394 and characterize vent product composition.
- Determine validity of scale-up parameters for use in extrapolation from Reactor 394 to production scale reactor.

2. Intermediate Dichlorosilane Reactor Development (3.2)
 - Operational parameters required to demonstrate a high deposition rate consistent with EPSDU requirements will be identified.
 - Design trade-off in reactor configuration/power supplying, and operational considerations will be conducted based on reactor requirements.
3. Dichlorosilane Process/Product Evaluation (3.3)
 - Complete characterization of liquid phase redistribution process.
 - Analyze purity of products of vapor phase redistribution.
 - Continue characterization of catalyst.
 - Complete dichlorosilane PDU (mini-plant) design and order long lead time items.
 - Initiate PDU construction.
4. Preliminary EPSDU Design (3.4)
 - Update mass balance as additional reactor data becomes available.
 - Begin development of process flow diagrams.

6.0 New Technology

No new technology was developed during this quarter.

7.0 References

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8.0 Acknowledgements

Appreciation is extended to N. Deitering, L. Ellis, D. Goffnett, L. Jones and H. Smith of Hemlock Semiconductor for their able assistance in the experimental aspects of the project. We further wish to acknowledge contributions in the area of project safety by R. Siegel, R. Salinger, T. Elvey and D. Parsels of Dow Corning Corporation.

APPENDICIES A

TABLE 1. SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE
USING TRICHLOROSILANE FEED

Run #	Rod Diameter mm	Silicon Fed (gh^{-1})	Silicon Deposition ($\text{gh}^{-1}\text{cm}^{-1}$)	Conv. Eff %
394-049-1	3.0-22.5	322	0.310	16.1
394-050-1	3.0-22.5	322	0.328	17.1
394-051-1	3.0- 9.0	265	0.234	14.8
394-051-2	9.0-20.0	891	0.508	9.6
394-051-3	20.0-26.5	672	0.615	15.3
394-051-4	26.5-30.5	672	0.624	15.6
394-052-1	3.0-28.0	571	0.433	12.7
394-053-1	3.0- 9.5	322	0.248	12.9

TABLE 2: SUMMARY OF EXPERIMENTAL REACTOR PERFORMANCE
USING DICHLOROSILANE FEED

Run #	Rod Diameter mm	Silicon Fed (gh^{-1})	Silicon Deposition ($\text{gh}^{-1}\text{cm}^{-1}$)	Conv. Eff. %
394-044*	3.0-11.0	322	0.619	32.2
394-049-2	22.5-28.0	322	0.668	34.5
394-050-2	22.5-32.0	616	1.175	32.0
394-051-5	30.5-34.5	322	0.611	31.8
394-052 ⁺ -2	28.0-33.5	322	0.777	40.4
394-052-3	33.5-38.0	322	0.737	38.3
394-052-4	38.0-41.5	322	0.727	37.8

* grown before start of contract

+ improved temperature control on dichlorosilane cylinder

TABLE 3. EFFECTIVENESS OF VARIOUS DRYING METHODS
FOR DOWEX MWA-1

<u>Run No.</u>	<u>Drying Method</u>	<u>Weight Loss (%)</u>
C-040-1	Trichloroethylene	50.0
C-040-2	Acetone	51.8
C-040-3	Methanol	50.9
C-040-4	Hexanes	51.3
C-041-1	Vacuum	51.0
C-042	Dry Argon Purge	50.6
C-043	Dessication Over Ca-Chloride	28.6

TABLE 4. THERMAL DECOMPOSITION PRODUCTS
OF DOWEX MWA-1

<u>Run No.</u>	<u>Temperature (°C)</u>	<u>Decomposition Mole %</u>	<u>Decomposition Products</u>
C-046	80-85 (7 hrs)	0.32	Trimethylamine
C-047	100-110(8 hrs)	0.40	"
C-049	120-130(6 hrs)	0.35	"
C-050	150-160(8 hrs)	1.1	"
C-054	135-145(7 hrs)	0.08	"

TABLE 5. THERMAL DECOMPOSITION CHARACTERISTICS
OF DOWEX MWA-1

<u>Run No.</u>	<u>Temperature (°C)</u>	<u>Weight Loss (%)</u>
C-041-1	Room (49 hrs.)	51.0 (moisture)
C-041-2	71 (24 hrs.)	0.36
C-041-3	89 (70 hrs.)	0.01
C-041-4	108 (93 hrs.)	0.28
C-041-5	147 (23 hrs.)	1.4
C-041-6	189 (20 hrs.)	6.2

APPENDICES B

FIGURE 1. SCHEDULE OF EFFORTS BY PHASES

FIGURE 2. SCHEMATIC OF CURRENT TRICHLOROSILANE BASED CVD PROCESS

FIGURE 4. EQUILIBRIUM RELATIONSHIPS FOR SILICON GENERATION FROM CHLOROSILANES AT 1050°C

Theoretical and experimental efficiencies of deposition of silicon from SiCl_2H_2 , SiCl_3H , and SiCl_4 in temperature interval of $1000^\circ\text{--}1300^\circ\text{K}$, $\text{Cl}/\text{H} \approx 10^{-1}$ in all cases.

FIGURE 5. SILICON DEPOSITION EFFICIENCIES
V. Ban (Ref. 3)

FIGURE 6. VENT COMPOSITION RELATIONSHIPS FOR SILICON
PRODUCTION FROM SiH_2Cl_2

FIGURE 7. SCHEMATIC OF HSC LOW COST DICHLOROSILANE BASED POLYCRYSTALLINE SILICON PROCESS

FIGURE 8. PROGRAM PLAN MILESTONE SCHEDULE (cont.)

FIGURE 8. PROGRAM PLAN MILESTONE SCHEDULE

FIGURE 9. SCHEMATIC OF REACTOR FEED AND VENT PIPING

FIGURE 10. SCHEMATIC OF REARRANGER PIPING

FIGURE 11. SCHEMATIC OF DICHLOROSILANE CYLINDER PIPING

FIGURE 12. SCHEMATIC OF BENDIX GAS CHROMATOGRAPH CONNECTION TO REACTOR 394 AND DATA PROCESSING SYSTEM

FIGURE 13. CHROMATOGRAPHIC DATA FROM DICHLOROSILANE-TO-SILICON RUN #394-044

FIGURE 14. CHROMATOGRAPHIC DATA FROM DICHLOROSILANE-TO-SILICON (Run #394-052-2)

CODES

(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	(F) Filter	□ Rotameter

FIGURE 15. SCHEMATIC OF LABORATORY TRICHLOROSILANE REARRANGER UNIT

FIGURE 16. SCHEMATIC OF DICHLOROSILANE PREPARATION UNIT
WITH MONOCHLOROSILANE SUPPRESSION

FIGURE 17. SCHEMATIC OF DICHLOROSILANE PREPARATION UNIT WITH MONOCHLOROSILANE REMOVAL

FIGURE 18. SCHEMATIC OF DICHLOROSILANE MINI-PLANT

HYDROGENATION

REDISTRIBUTION

DECOMPOSITION

Figures in parentheses are recycled material

FIGURE 19. PRELIMINARY MOLAR MATERIAL BALANCE FOR HSC DICHLOROSILANE PROCESS