A LOW-COST POLYSILICON PROCESS BASED ON THE SYNTHESIS AND DECOMPOSITION OF DICHLOROSILANE

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ABSTRACT

Major process steps of a dichlorosilane based chemical vapor deposition (CVD) process for the production of polycrystalline silicon have been evaluated. While an economic analysis of the process indicates that it is not capable of meeting JPL/DOE price objectives ($14.00/kg in 1980 dollars), product price in the $19.00/kg to $25.00/kg range may be achieved. Product quality has been evaluated and ascertained to be comparable to semiconductor-grade polycrystalline silicon. Solar cells fabricated from the material are also equivalent to those fabricated from semiconductor-grade polycrystalline silicon.

I. INTRODUCTION

Widespread penetration of the large U.S. residential power market by photovoltaic power generation requires an extremely low array price. Preliminary analysis of the cost structure encountered in photovoltaic array manufacturing, as part of a design-to-cost strategy, assigned cost targets for each major component of array manufacturing.[1] This exercise resulted in a cost target of $10/kg (1975 dollars) being assigned to the basic raw material used in the manufacture of silicon solar cells; polycrystalline silicon. This cost target was based on the polycystalline silicon being used to produce a 10% efficient solar cell and was approximately one-seventh the material market price at that time.[2]

The extremely low polycrystalline cost allocation established for the Low-Cost Silicon Solar Array program supported by The Department of Energy, in effect, removed from consideration for government support Siemens-type chemical vapor deposition (CVD) processes. As the LSSA program progressed, it became apparent that solar cell efficiency was a strong driving force in reducing array power cost and that minute impurity concentration in the polycrystalline silicon could result in substantial degradation of cell performance.[3,4,5]

Analysis of the value which could be placed on a feedstock material, if it provided improved solar cell efficiency, coupled with favorable results obtained at Dow Corning Corporation regarding use of dichlorosilane as a CVD reactor feedstock resulted in formulation of the Hemlock Semiconductor Dichlorosilane Based CVD Process. The analysis indicating that a premium price may be warranted for a material capable of producing improved cell efficiency is contained in Section II. Section III is devoted to a description of the HSC Dichlorosilane Based CVD Process and contrasts this process to the current polycrystalline silicon production process used in the manufacture of semiconductor-grade material. Results of a major process development program to demonstrate both the production and decomposition of dichlorosilane in production-scale equipment are discussed in Section IV.

A basic claim for this process is that it would result in a reduction in manufacturing cost when compared to current technology, while providing a product of comparable quality to semiconductor-grade material. Analytical data on the purity of polycrystalline silicon produced by dichlorosilane decomposition is presented in Section V.

II. THE VALUE OF SOLAR CELL EFFICIENCY

Early in the JPL/DOE Large Scale Solar Array Program expressions were developed relating the cost per peak watt ($\$/W_{pk}$) of array power to the cost per peak watt of the major cost components. Major cost components considered in these analyses consist of polycrystalline silicon cost, $(\$/W_{pk})_{Si}$; cost added for sheet (wafer) fabrication, $(\$/W_{pk})_{wafer}$; added cost for cell fabrication, $(\$/W_{pk})_{fab}$; cost of encapsulant, $(\$/W_{pk})_{encp}$; and, finally, the cost of array assembly and testing, $(\$/W_{pk})_{A\&T}$. Total cost of peak power may then be expressed in terms of component costs as in equation (1)[6]

$$(\$/W_p)_{array} = (\$/W_{pk})_{Si}+(\$/W_{pk})_{waf}+(\$/W_{pk})_{fab}+(\$/W_{pk})_{encp}+(\$/W_{pk})_{A\&T} \quad (1)$$

Values for the component costs developed elsewhere may be expressed as

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$$(\$/W_{pk})_{Si} = \$/kg\ Si\ {*}(t{*}U{*}D)/(I{*}\eta_e{*}Y_w{*}Y_{etch}{*}Y_{mfg})$$
$$(\$/W_{pk})_{waf} = (\$/M^2)_{wafer}/(I{*}\eta_e{*}Y_{mfg})$$
$$(\$/W_{pk})_{fab} = (\$/M^2)_{cell}/(I{*}\eta_e)$$
$$(\$/W_{pk})_{encp} = (\$/M^2)_{mod}/(I{*}\eta_e{*}\eta_p)$$
$$(\$/W_{pk})_{A\&T} = (\$/M^2)_{mod}/(I{*}\eta_e{*}\eta_p)$$

where

I = Insolation = 100 w/m^2
D = Density of silicon = 2.3 g/cm^3
U = Conversion factor for (1/1000) inch to meter
η_e = Encapsulated cell efficiency
η_p = Packing efficiency
t = Cell thickness (1/1000 inch)
Y_w = Silicon to wafer yield
Y_{etch} = Silicon yield through cell processing
Y_{mfg} = Cell yield from wafers through finished modules

Using equation (1), array peak power cost (1980 dollars) has been calculated as a function of efficiency for polycrystalline silicon costs of \$14/kg, \$28/kg, and \$42/kg. Sheet technology was assumed with other parameters in equation (1) having the following values

$$\eta_p=0.92; t=10 \text{ mils};\ Y_w=0.9\ Y_{etch}=0.9;\ Y_{mfg}=0.95;$$

Figure 1 illustrates the dependence of array peak power cost (\$/W_{pk}) on cell efficiency. As shown in Figure 1, the DOE objective of \$0.70/watt can be met with an 11.5% efficient cell using \$14/kg polycrystalline silicon. However, the power cost objective can also be met with higher priced feedstock material provided cell efficiency is higher (i.e. a doubling in feedstock material cost is cost effective provided it results in a cell of 12.5% efficiency).

The value placed on efficiency by equation (1) and illustrated in Figure 1 does not include the cost of array installation which is also area dependent. Equation (1), thus, expresses the value of high-efficiency cell performance conservatively since it neglects these installation costs.

III. HSC DICHLOROSILANE BASED CVD PROCESS

Chemical vapor deposition of high-purity polycrystalline silicon from trichlorosilane (TCS) feedstock forms the basis of the semiconductor-grade polycrystalline silicon industry. Material produced by this process meets the stringent quality requirements of the electronics industry at an acceptable price and meets or exceeds the quality requirements of the emerging silicon solar array industry. Although process improvements, coupled with expanding capacity, have resulted in steadily declining polycrystalline silicon prices (in constant dollars), basic process changes are required to achieve the dramatic cost reduction required to support widespread commercialization of photovoltaic power generation. The current process employed in the manufacture of polycrystalline silicon is shown schematically in Figure 2. Major production processes include: hydrochlorination of metallurgical-grade silicon to produce trichlorosilane, trichlorosilane purification, reductive chemical vapor decomposition of trichlorosilane to produce high-purity silicon rods, and by-product recovery and recycle.

While the ability of the process to produce material of adequate quality for photovoltaic use is unquestioned, process shortcomings are associated with

1) High power consumption at the CVD reactor.

2) Large silicon tetrachloride (STC) by-product stream.

3) Poor efficiency in both silicon and chlorine usage.

4) Low conversion efficiency of silicon in the CVD process resulting in large capital costs in the deposition/recovery system.[7]

The HSC dichlorosilane based CVD process addresses all of the above problem areas. The process, as envisioned for a stand- alone plant is shown schematically in Figure 3. Hydrogenation of silcon tetrachloride in a metallurgical-grade silicon fluidized bed is used to produce trichlorosilane. Standard purification methods are employed to produce high-purity trichlorosilane. Dichlorosilane is produced via the catalyzed redistribution of trichlorosilane while silicon tetrachloride, the by-product of this reaction, is recycled through the hydrogenation process. High-purity dichlorosilane is decomposed in a rod-type CVD reactor and all reaction products with the exception of hydrogen chloride are recycled. The hydrogen chloride is, of course, of value for use in the hydrochlorination process discussed previously. The major chemical reactions occurring may be summarized as:

Hydrogenation of Silicon Tetrachloride

$$SiCl_4 + H_2 + Si \rightleftharpoons HSiCl_3\ (+\ H_2 + SiCl_4)$$

Dichlorosilane Synthesis

$$2HSiCl_3 \overset{\text{Catalyst}}{\rightleftharpoons} H_2SiCl_2 + SiCl_4$$

Dichlorosilane Decomposition

$$H_2SiCl_2 + H_2 \rightleftharpoons Si + (H_2 + H_2SiCl_2 + HSiCl_3 + SiCl_4 + HCl)$$

Key to the success of the process is the advantages associated with the use of dichlorosilane as a feedstock for the CVD reactor and the hydrogenation of silicon tetrachloride. With regard to dichlorosilane, it is less stable than trichlorosilane both thermodynamically and kinetically.

In thermodynamic terms, dichlorosilane is a substantially better source of silicon than trichlorosilane. A perspective on equilibrium relationships between the two chlorosilanes is presented in Figure 4.[8] 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 percent conversion into silicon for a range of feed compositions (Cl/H ratios), since

$$\text{Percent Conversion} = \frac{(\text{Si/Cl})_{in} - (\text{Si/Cl})_{out}}{(\text{Si/Cl})_{in}}$$

At a feed of 10 mole percent dichlorosilane in H_2 and a temperature of 1050°C, for example,

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

Conversion efficiency of trichlorosilane under the same conditions is only 37%.

A further thermodynamic advantage of dichlorosilane relative to trichlorosilane is its lower sensitivity to increases in reactant concentration. For trichlorosilane, doubling the mole percent 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 the anticipated CVD processes, 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, respectively. Conditions utilized in epitaxial reactors typically involve substantially lower mole percent chlorosilane and flow rates than the polysilicon production process. However, work by Ban of RCA Laboratories has been conducted at mole fractions and temperatures compatible with the polycrystalline silicon production process.[9] Ban's results indicate that under conditions in which silicon tetrachloride and trichlorosilane are far from equilibrium, dichlorosilane has achieved equilibrium.

The high conversion efficiency associated with dichlorosilane decomposition results in increased deposition rate and reduced power consumption per unit of time. Specific goals of the government supported effort were to achieve a conversion efficiency of 40 mole percent, a deposition rate of 2.0 $gh^{-1}cm^{-1}$[+] and a power consumption at the reactor of less than 60 kWh/kg. The high conversion efficiency, coupled with the lower molar chlorine content, also results in a substantially reduced recovery system size per kg of silicon produced thus reducing capital costs.

IV. PROCESS PERFORMANCE

The following major areas associated with overall process demonstration were investigated:

1) Evaluation of hazards of dichlorosilane and its use as a reactor feedstock.
2) Evaluation of suitable catalysts for use in synthesis of dichlorosilane via redistribution of trichlorosilane.
3) Decomposition characteristics of dichlorosilane in a laboratory-scale CVD reactor.
4) Evaluation of scaled-up dichlorosilane production and decomposition processes.

Items 1, 2, and 3 have been discussed elsewhere.[10,11] This section will be devoted to a discussion of the scaled-up process demonstration unit and a summary of reactor performance at the pilot scale.

Prior to operation of large CVD reactors, optimization experiments utilizing a two-level experimental design were conducted in a 12-inch diameter experimental reactor to establish quantitative correlation between reactor operating parameters (total flow rate, mole percent dichlorosilane, and temperature) and measured responses (silicon deposition rate, conversion, and power consumption). Eight sets of operating conditions (1-8) which correspond to the corners of a cube in which the edges represent the variables: flow, mole percent DCS, and temperature were investigated. Feed and vent gas compositions were analyzed using a Bendix Model 170 gas chromatograph, a Perkin-Elmer Sigma 10 data system, and a North Star Horizon micro-computer.

Polynomial expressions describing the relationship between operating parameters and responses were developed using a least squares multiple regression analysis program. Any response can be predicted if the operating conditions are within the limits set for the experimental design. The order of importance of the variables on the response function is summarized in Table 1.

Following success in the experimental CVD reactor and in dichlorosilane production via base catalyzed redistribution of trichlorosilane in the laboratory, an integrated scaled-up dichlorosilane production/chemical vapor deposition system was constructed and evaluated. A schematic of this process demonstration unit (PDU) is shown in Figure 5.

In the PDU, trichlorosilane is preheated prior to entering the redistribution reactor filled with Dowex® MWA-1[*]. The resulting chlorosilane mixture is distilled in a packed distillation column. The overhead product (97% DCS) is mixed with hydrogen for transport to the CVD

[+] Deposition rate is expressed in grams per hour per unit length of substrate.

[*] Manufactured by Dow Chemical Co., Midland, MI

reactors. The bottoms by-product of the distillation column (trichlorosilane and silicon tetrachloride) is sent to the Hemlock Semiconductor vent recovery system.

Results from the experimental design were verified by data collected using modified production reactors. The measured responses of deposition rate, conversion efficiency, and power consumption for both reactor types (experimental and modified production) are compared in Table 2 with the original program goals.

The deposition rate goal of 2.0 $gh^{-1}cm^{-1}$ was achieved with the process demonstration unit during the current phase of the program. Conversion efficiency remains approximately 10% below the goal established, but this shortcoming is not viewed as a serious problem since conversion efficiency is reactor size dependent. Power consumption remains higher than desirable and represents the major problem area, even though it is substantially below values reported for systems using trichlorosilane feedstock.

V. POLYCRYSTALLINE SILICON PRODUCT PURITY

Product quality, in addition to manufacturing cost reduction, is key to the success of a dichlorosilane based CVD process meeting future photovoltaic material needs. Material produced in demonstrating the dichlorosilane process feasibility was given the same analytical scrutiny as semiconductor-grade material produced at HSC. Data for approximately 150 deposition reactor runs indicates an average boron concentration of 0.1 ppba, an average donor concentration of 0.5 ppba, and an average carbon concentration of 0.3 ppma.

Boron, donor, and carbon concentrations are all comparable to specification for semiconductor-grade material. Mass spectrographic analysis of selected samples for other trace impurities resulted in measured impurity concentrations at or below the detection limit of the instrument and no significant difference could be detected between polycrystalline silicon grown from dichlorosilane and that deposited from semiconductor-grade trichlorosilane.

Single crystal ingots were prepared at HSC via Czochralski crystal growth and forwarded to Westinghouse Research Laboratory and the Jet Propulsion Laboratory for solar cell processing and evaluation. Cells fabricated at Westinghouse Research Laboratory were not AR coated, while cells fabricated for the Jet Propulsion Laboratory by Applied Solar Energy Corporation were fully processed. Performance characteristics of both sets of cells are summarized in Table 3. Cells fabricated by Westinghouse using DCS material were on an average 2.3% more efficient than baseline cells, while cells fabricated by Applied Solar Energy Corporation using DCS material were on an average 3.5% more efficient than baseline cells.

CONCLUSIONS

The strong dependence of solar array power cost on cell efficiency may justify use of extremely high quality polycrystalline silicon even at a premium price. A process for the production of such a high quality material at a price substantially below current market price has been developed and key segments of process technology demonstrated at the pilot plant stage. Material evaluations through solar cell fabrication indicate this material to be equivalent to current semiconductor-grade polycrystalline silicon quality standards. Additional reactor development-related work should result in further improvements in CVD reactor performance and product quality.

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TABLE 1. Relative Importance of Independent Variables on Response Function in Dichlorosilane Decomposition.

Silicon Deposition Rate	Conversion Efficiency	Power Consumption
1. Flow	1. % DCS	1. Flow
2. Temp.	2. Temp.	2. % DCS
3. % DCS	3. Flow	3. Int. of Temp. X % DCS
4. Int. of Flow and Temp.	4. Int. of Temp. and % DCS	4. Temp.
5. Int. of Flow and % DCS	5. Int. of Flow and Temp.	5. Int. of Flow and Temp.
6. Int. of Temp. and % DCS	6. Int. of Flow and % DCS	6. Int. of Flow and % DCS

TABLE 2. Comparison of Experimental Reactor and Pilot Scale Reactor Performance with JPL/DOE Contract Goals.

	Deposition Rate $gh^{-1}cm^{-1}$	Conversion Mole Percent	Power Consumption kWh/kg
JPL/DOE Goal	2.00	40	60
Experimental Design	1.60	35.2	96
Modified Production Reactor	2.00	35.1	82

TABLE 3. Summary of Solar Cell Performance Using Dichlorosilane

Cell Designation	V_{oc} (Ave.) mV	I_{sc} (Ave.) mA/cm^2	CFF (Ave.) %	η (Ave.) %
Applied Solar DCS	590	29.0	75	12.84
Applied Solar Baseline	583	28.2	75	12.40
Westinghouse DCS	571	21.18	70	9.11
Westinghouse Baseline	553	21.10	71	8.9

FIGURE 1.
DEPENDENCE OF ARRAY POWER COST (DOLLARS/WATT PEAK) ON SOLAR CELL EFFICIENCY AND POLYCRYSTALLINE SILICON COST

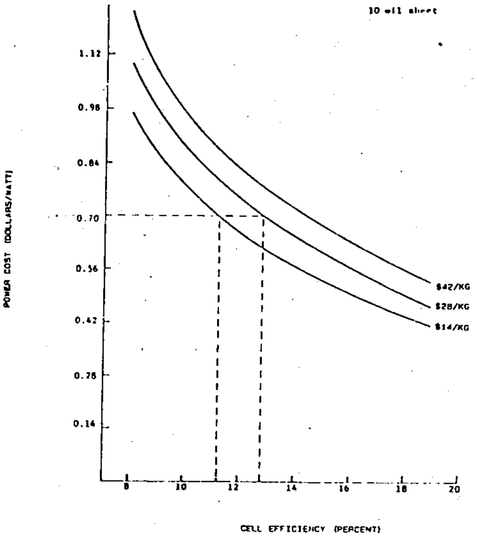

FIGURE 2
PROCESS FLOW DIAGRAM OF PROCESS CURRENTLY USED FOR THE PRODUCTION OF POLYCRYSTALLINE SILICON

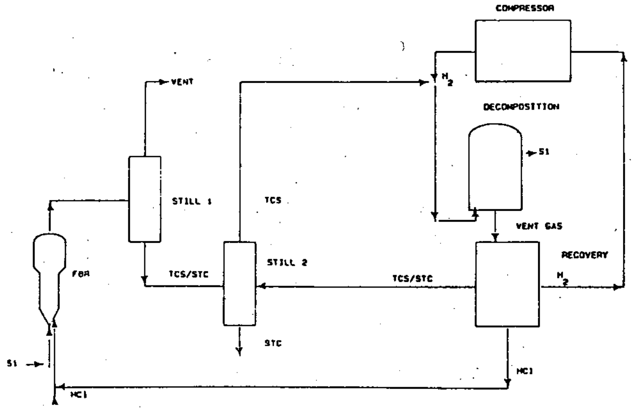

FIGURE 3
PROCESS FLOW DIAGRAM FOR HEMLOCK SEMICONDUCTOR DICHLOROSILANE BASED CVD PROCESS

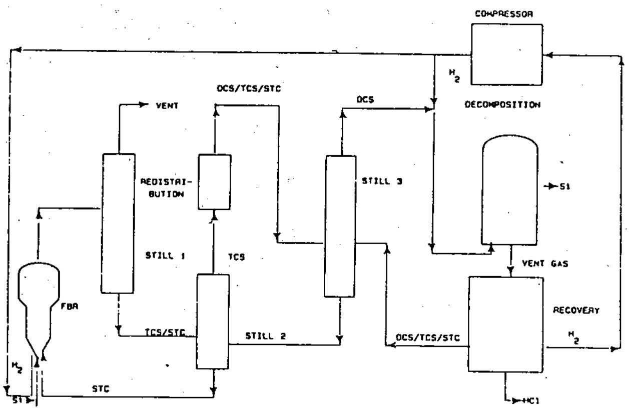

FIGURE 4
EQUILIBRIUM RELATIONSHIPS FOR SILICON GENERATION FROM THE HYDROGEN-SILICON-CHLORINE SYSTEM AT 1050°C

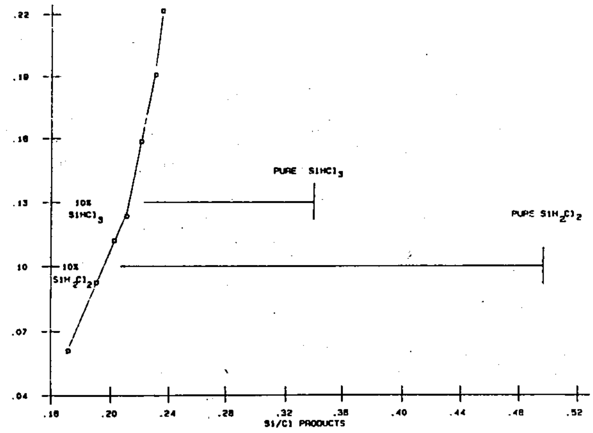

FIGURE 5
SCHEMATIC DIAGRAM OF A SMALL CVD REACTOR FOR DICHLOROSILANE DECOMPOSITION