

5230-12  
Photovoltaics Program  
Program Analysis and Integration Center

DOE/ET-20356-17  
Distribution Category UC-63

(NASA-CR-173897) POLYCRYSTALLINE SILICON N84-33213  
STUDY: LOW-COST SILICON REFINING TECHNOLOGY  
PROSPECTS AND SEMICONDUCTOR-GRADE  
POLYCRYSTALLINE SILICON AVAILABILITY THROUGH 1988 (Jet Propulsion Lab.) 46 p  
Unclas  
G3/76 23832

## Polycrystalline Silicon Study

Low-Cost Silicon Refining Technology Prospects  
and Semiconductor-Grade Polycrystalline Silicon  
Availability through 1988

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May 30, 1984

Prepared for  
U.S. Department of Energy  
Through an Agreement with  
National Aeronautics and Space Administration  
by  
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The JPL Flat-Plate Solar Array Project is sponsored by the U.S. Department of  
Energy and is part of the Photovoltaic Energy Systems Program to initiate a  
major effort toward the development of cost-competitive solar arrays.

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This publication reports on work done under NASA Task RE-152, Amendment  
200, DOE/NASA IAA No. DE-AC01-76ET20356.

## ABSTRACT

Photovoltaic arrays that convert solar energy into electrical energy can become a cost-effective bulk energy generation alternative, provided that an adequate supply of low-cost materials is available. One of the key requirements for economic photovoltaic cells is reasonably priced silicon.

At present, the photovoltaic industry is dependent upon polycrystalline silicon refined by the Siemens process primarily for integrated circuits, power devices, and discrete semiconductor devices. This dependency is expected to continue until the DOE-sponsored low-cost silicon refining technology developments have matured to the point where they are in commercial use. The photovoltaic industry can then develop its own source of supply.

Since 1979 the Jet Propulsion Laboratory Technology Development and Application Lead Center (TD&A), now the Program Analysis and Integration Center (PA&I), has periodically examined the availability of refined silicon and the status of the DOE-sponsored low-cost silicon refining technology developments. Three reports have been published, based on surveys conducted by JPL consultants in 1979, 1981, and 1983.

This report updates the silicon material availability and market pricing projections through 1988, based on data collected early in 1984. It also overviews the silicon refining industry plans to meet the increasing demands of the semiconductor device and photovoltaic product industries. A section of the report has been devoted to review of the DOE-sponsored technology research for producing low-cost polycrystalline silicon, probabilistic cost analysis for the two most promising production processes for achieving the DOE cost goals, and the impacts of the DOE photovoltaics program silicon refining research upon the commercial polycrystalline silicon refining industry.

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## EXECUTIVE SUMMARY

Photovoltaic cell arrays that convert solar energy into electric energy can become a cost-effective bulk (grid-connected) energy source, provided that an adequate supply of low-priced materials is available and that automated fabrication techniques are used. A key material for photovoltaic arrays is silicon (Si), on which is based the most promising semiconductor material technology for achieving the long-term cost goals of the U.S. Department of Energy (DOE) National Photovoltaics Program.

At present, the photovoltaics (PV) industry depends upon the availability of semiconductor-grade polycrystalline silicon, which is produced primarily for integrated circuits, power devices, and discrete semiconductor devices. In most cases, the PV industry has used refined silicon rejects of the semiconductor device industry, which are of a slightly lower grade and, therefore, less expensive. This dependence is expected to continue until DOE-sponsored low-cost silicon refining process developments become commercial and provide the PV industry with a source of low-cost material.

Since 1979 the Jet Propulsion Laboratory (JPL) Photovoltaics Program Analysis and Integration Center (PA&I) has periodically evaluated the availability of refined silicon and the status of new technology developments. Silicon material outlook studies have been previously published to report on the status of the silicon refining industry and to predict silicon availability. In November 1979 a survey (Reference 1) concluded that a shortage of silicon material was developing because of steadily increasing consumption by the semiconductor products industry with no concomitant increase in production capacity. Such a shortage would have hurt the growth of the PV industry because the selling price of any available silicon material would have been too high for the PV industry to use. The published report was widely accepted by the silicon refining industry. It provided for them, for the first time, a complete review of the silicon material supply-and-demand situation, including data for the present and a forecast of the demand of the PV industry.

An apparent reason for the developing shortage was that the silicon refining industry had been concerned that the DOE-funded program to develop technology for low-cost polycrystalline production would lead to processes with substantial cost advantages, and thus production by the Siemens process would become less competitive. This concern led to a reluctance by the industry to invest in construction of new plants using the Siemens process. As the number of new technology options was narrowed to the two most promising contenders, the Union Carbide Corp. (UCC) silane process and the Hemlock Semiconductor Corp. modified Siemens process, the refining industry's concern for outmoding of the Siemens process abated.

The silicon industry is highly competitive, and is striving to reduce production cost. Intensive proprietary efforts were made to develop improvements in the Siemens process. As a result, modifications of the Siemens reactor and of the process for the preparation and purification of trichlorosilane have been installed in existing plants. These have led to decreased production costs, especially in electric energy use for deposition reactors. Throughput and material utilization efficiency have increased greatly through these changes.

In November 1980 a survey of the silicon refining industry (Reference 2) conducted by Remo Pellin, a JPL consultant, found that silicon availability had begun to change; however, this was not before some large fluctuations in the spot-market price had taken place. The spot-market price for silicon was quoted as high as \$140/kg in April 1980; the lowest 1980 spot-market price quoted was below \$50/kg.

Another update of the silicon availability analysis, conducted in December 1982 and January 1983 (Reference 3), indicated that the improved trend of adequate silicon supply for the photovoltaic and semiconductor industries was continuing. The conclusions of this survey were:

- 1) Semiconductor-grade polycrystalline silicon will be available to meet the market demands of the semiconductor industry although some transient situations of short supply may occur, depending on the rate of industry recovery from the recession experienced in 1980.
- 2) Lower-grade polycrystalline silicon (rejected by the semiconductor industry) would be available for the PV industry at the market price. This price might be more than the industry could afford to pay while continuing to reduce the price of the PV products in its strategy to accelerate market demands.

The subjects addressed in this report are: (1) a final survey of silicon material availability; the situation is considered to be well in hand, with industry aggressively maintaining supply near the demands; (2) technology status and expansion plans for the silicon refining industry; (3) a brief look at the polysilicon market pricing outlook, particularly for the photovoltaic industry, and (4) a status review of research funded by DOE for the development of low-cost processes for polysilicon production, and the effect of that research on the polysilicon industry.

The industry survey data were collected primarily by Remo Pellin, with assistance by James Lorenz, another JPL consultant. Additional input was provided and analyses were conducted by PA&I and Flat-Plate Solar Array Project (FSA) staff members.

The conclusions from the data collected are: (1) in the past, the demands of the semiconductor industry and the PV industry have been met by production capacity increases; additional production capacity increases are planned to meet the demand through 1988. Table 1 shows the totals of world capacity to manufacture semiconductor-grade polycrystalline silicon and of silicon usage. Although the data in Table 1 showed that the forecast plant capacity may be in excess of forecast demand, the expected production rate will be closely matched to the market demands, as has been the case in the past; (2) the silicon refining industry, as in the past, will continue to improve the Siemens refining process to reduce cost and improve product quality, and the entry of UCC into the polysilicon business will promote strong competition; (3) the market price of silicon will depend on the supply-and-demand situation, with sporadic high spot-market prices. The demand will be sensitive to growth rates of both the semiconductor and the PV industries.



Table 1. Polycrystalline Silicon: Historic and Forecast World Manufacturing Capacity, Plus Usage, Metric Tons per Year

Year	Capacity	Usage
1977	2395	1326
1978	2445	1668
1979	2740	2148
1980	3760	2312
1981	4410	2568
1982	5250	3092
1983	5794	4000
1984	6140	4970
1985	7900	5985
1986	9120	7310
1987	11020	8675
1988	12820	10566

The DOE-sponsored research program has had significant effects on the world's polysilicon production technology and production capacity. The decision for the commercialization of the silane process by UCC is a prime example of Government-sponsored, high-risk research yielding a promising result with rapid transfer to industry. UCC had considered entering the polysilicon business several times before 1980, but did not make the commitment until the feasibility of the silane process had been demonstrated in the DOE-funded, FSA-administered research program.

Today, and in the near future, most polycrystalline silicon will be manufactured by variants of the Siemens process. The modified Siemens process elements, developed by Hemlock with DOE funding, can ultimately reduce the production cost of all polycrystalline silicon produced by Siemens-type processes. Lower production cost in the modified Siemens processes and in commercialized low-cost processes is expected to influence the market price, which is expected to decrease gradually, depending on the supply/demand scenario. It can be said that the DOE-sponsored low-cost silicon refining research is one area in which the United States, through proper use of Government resources, has maintained technology leadership. FSA silicon refining research has initiated industry action and focused attention on this critical polysilicon technology.

#### Executive Summary References

1. Costogue, E., et al, Silicon Material Outlook for 1980-1985, JPL Publication 79-110, Jet Propulsion Laboratory, Pasadena, California, November 1, 1979.
2. Costogue, E., et al, Industry Survey Report Status of Silicon Material and Silicon Sheet Techniques, JPL Internal Document No. 5230-5, Jet Propulsion Laboratory, Pasadena, California, May 1, 1981.
3. Costogue, E., et al, Polycrystalline Silicon Material Availability and Market Pricing Outlook Study for 1980 to 1988, JPL Publication 83-9, Jet Propulsion Laboratory, Pasadena, California, February 1983.

## SECTION I

### INTRODUCTION

The practicality of photovoltaic (PV) arrays as an energy source depends upon its energy selling price compared with that of other energy sources. Because semiconductor-grade polycrystalline silicon (Si) is almost universally used as the prime material for the manufacture of photovoltaic arrays, the availability of a large quantity of relatively low-cost semiconductor-grade polycrystalline silicon is critical.

At present, the photovoltaics industry depends upon the availability of semiconductor-grade polycrystalline silicon, which is produced for the semiconductor industry and is used primarily for integrated circuits, power devices, and discrete semiconductor devices. This is expected to be the primary source until DOE-sponsored research provides the technology for low-cost processes and the refining industry installs production capacity based on this technology.

The Jet Propulsion Laboratory's (JPL's) Photovoltaics Program Analysis and Integration Center (PA&I) has tracked the availability of the silicon material (critical for development of the photovoltaics industry) and has periodically reported survey results.

A report titled Silicon Material Outlook for 1980-1985 (Reference 1) was published in November 1979 by the JPL Technology Development and Applications (TD&A) Lead Center. It described the results of a survey conducted in July 1979. The survey team reached the following conclusions:

- (1) A severe shortage could occur in 1980 due to increased consumption by the semiconductor products industry and by the emerging photovoltaics industry. Very little expansion of the production capacity using existing technology was expected during this period because of the prospect of the new low-cost refining technology under development by the DOE photovoltaics program.
- (2) As a result, a seller's market would be created and the price of silicon would increase.

In November 1980 (Reference 2), a silicon industry survey update was conducted by a JPL consultant, Remo Pellin. It was concluded that the silicon market outlook was beginning to change significantly. However, before that, some large fluctuations in spot-market pricing had taken place. In April 1980, the spot-market price for silicon was quoted as high as \$140/kg (Reference 3), an increase of a factor of two from the spot-market prices quoted in 1979. The survey data were summarized in a report titled Industry Survey Report Status of Silicon Material and Silicon Sheet Techniques (Reference 2), with the following conclusions:

- (1) No long-term shortage of semiconductor-grade polycrystalline silicon would occur and the needs of the semiconductor products industry would be met. This improved supply outlook was the

response of the polysilicon refining industry to the forecast shortfall. The industry had begun to increase plant capacity in 1980, primarily by process improvements of existing plants.

- (2) Excess semiconductor-grade silicon and non-conforming silicon rejected by the semiconductor device industry would be available for the photovoltaics industry.

Another survey of refined silicon availability with emphasis on market pricing was conducted early in 1983. A report titled Polycrystalline Silicon Material Availability and Market Pricing Outlook Study for 1980 to 1988 was published in February 1983 (Reference 4). Its conclusions were:

- (1) Polycrystalline silicon availability is now, and will continue to be, in excess of users' demands.
- (2) Polycrystalline silicon prices have decreased over the past year and will continue to drop as the modernization of Siemens process plants proceeds and new technology plants begin to enter the market.
- (3) Greatly expanded plant capacity has been achieved with minimal capital expenditures through process improvements.
- (4) The present and the projected overcapacities have led to more aggressive process cost-reduction efforts, increased yields, and competitive pricing.
- (5) The worldwide recession, which began in the summer of 1980, has caused a slightly lower rate of growth in the semiconductor device industry than was expected.
- (6) New low-cost refining processes, largely developed through DOE-funded programs administered by JPL, are reaching technology readiness. In addition, improvements of the existing Siemens process plants are expected to be available; these will further reduce the refining cost and hence the selling price.

This report, in addition to updating information on semiconductor-grade polycrystalline silicon availability and selling-price projections, reviews DOE research program efforts to develop low-cost polysilicon refining processes for photovoltaic use, and attempts to assess the impact of the program achievements on the polysilicon industry.

## SECTION II

### SILICON MARKETPLACE

#### A. POLYCRYSTALLINE SILICON OUTLOOK

Silicon solar cells are manufactured from single-crystal wafers, polycrystalline wafers, ribbons, or amorphous silicon thin films. The cost of the polycrystalline silicon currently constitutes about 10% to 15% of the manufacturing cost of a typical photovoltaic module (\$0.60 to \$0.90 out of \$6 per peak watt). The use of semiconductor-grade polycrystalline silicon allows the manufacture of highly efficient single-crystal solar cells, reducing the overall cost of the module and support structure per peak watt.

It has been concluded that the use of any special "solar-grade" polycrystalline silicon, which results in noticeably less efficient solar cells, is not warranted, as the program emphasis is on high efficiency. Thus, the silicon solar-cell industry depends for supply on the same polycrystalline silicon as does the semiconductor industry. For the near future, as in the past, the silicon solar cell industry will be able to obtain and use rejected polycrystalline silicon. This rejected silicon consists of virgin material that does not meet integrated-circuit impurity content specifications for such elements as boron, phosphorus, or carbon; this rejected silicon is as much as 5% of all semiconductor-grade silicon produced. In general, solar cells with satisfactory efficiency can be fabricated from this silicon.

Major changes in the semiconductor-grade polycrystalline silicon market occurred in 1983. In January 1983 the semiconductor product industry began a mild recovery from the 1981-1982 world recession. During June 1983 the recession suddenly ended in the integrated circuit product industry and panic buying began (Reference 5). This sales boom continued through March 1984 and is expected to extend at least through 1985 (Reference 5).

As a result of this boom in the sales of integrated circuits, orders for polished silicon wafers increased by 50% between July 1983 and December 1983. Only the presence of a significant unused capacity for the production of polished silicon wafers prevented panic buying of this product. The annual world capacity for the manufacture of polished silicon wafers was 1.5 billion square inches in early 1984. The projected demand is expected to be 1.1 billion square inches in 1984 and 1.385 billion square inches in 1985. Expansion of wafer manufacturing capacity is relatively easy, and new wafer plants can be built in 12 to 15 months. No shortage of polished wafers is expected through 1990. Indications are that the expected wafer manufacturing increases will take place primarily in four companies, only one of which is in the United States: Wacker Chemetronic GmbH, Monsanto Co., Shin-Etsu Handotai, and Osaka Titanium Mfg. Co.

The use of semiconductor-grade polycrystalline silicon has grown commensurately with the increase in use of polished silicon wafers. In March 1984 the polycrystalline silicon demand and production were balanced (Reference 6). Even though production capacity is expanding, some experts currently believe that a shortage of polycrystalline silicon could occur in

1985 (Reference 7). The reasoning is that at least three years are required to build silicon refining plants. A careful analysis, however, reveals that the production capacity, comprising existing plants, plants being built, and plants in the planning stage, should provide sufficient polycrystalline silicon to meet the forecast demand, at least through 1988. Accordingly, it is expected that prices for polycrystalline silicon will slowly decline without large transients over this period because of competitive pressures, large-scale manufacture, and new-technology plants beginning operation.

Various factors in the production and use of polycrystalline silicon require some explanation. Contrary to the normal business cycle, at the beginning of the recession recovery period in the second half of 1983, increases in polycrystalline purchases were larger than expected. It is expected that this increase will soon settle back to a normal rate. Several months are usually required to convert polycrystalline silicon into integrated circuits; business cycles seldom are predictable beyond six months. Thus, buying requests normally increase at the start of the boom period and slow down at the end of it. Hence, raw materials are always more difficult to purchase at the start of a boom business cycle. In the usual business practice, raw material inventories are increased substantially above steady state. These factors virtually ensure that some panic buying of raw materials will occur, and this has occurred for polycrystalline silicon during the past six months.

The capacity of a polycrystalline silicon plant should be considered to be variable. For example, both Wacker and Hemlock Semiconductor Corp. have demonstrated that the capacity of an existing plant can be doubled by process changes alone. This has been done by introducing the reactants at a higher rate, by increasing the average rod diameter of produced polycrystalline silicon, and by increasing the deposition temperature. These parametric adjustments can be made to increase capacity of existing plants during times of high demand.

To predict the status of the polycrystalline silicon market in future years, an analysis must be made of both the market demand and manufacturing capacity.

Table 2-1, first published in Silicon Materials Outlook Study, An Update on January 24, 1983 (Reference 4), has been revised to show correctly the usage of non-solar-cell silicon electronic devices, silicon wafers, silicon single crystals, and electronic-grade polycrystalline silicon, and usage projections over the years from 1974 to 1988. The premises used in the construction of this table are discussed thoroughly in Reference 4. Corrections were also necessary to reflect lower yields for the Japanese Shin-Etsu Handotai and Osaka Titanium companies in converting polycrystalline silicon to polished silicon wafers; the Japanese yield is approximately 35% versus 50% for both Wacker and Monsanto. However, the Japanese share of the world market is increasing significantly because of the high wafer quality they supply as a result of their stringent product specifications. Based on Table 2-1 data, polycrystalline silicon use will continue to increase from approximately 4,000 metric tons in 1984 to more than 10,000 metric tons in 1988. Although boom and recession business cycles are difficult to predict and the exact yearly usage may vary from Table 2-1, the overall growth projection of about 20% per year is reasonable through 1988.

Table 2-1. A Free-World Forecast of Silicon Material Usage

Year	Silicon Device Usage, \$x10 <sup>6</sup>	Material Value, %	Silicon Wafer Value, \$x10 <sup>6</sup>	Average Value per in. <sup>2</sup> , \$	Silicon Wafers, in. <sup>2</sup>	Average Diameter Of Crystal, in.	Grams of Polysilicon per in. <sup>2</sup> of Wafer	Single- Crystal Silicon, Metric Tons	Polysilicon, Metric Tons
1974	5,750	4.17	234	0.75	312	2.8	2.79	522	871
1975	5,170	4.17	230	0.75	307	2.9	3.00	553	921
1976	6,545	4.17	294	0.75	392	3.0	2.99	702	1170
1977	8,610	4.17	373	0.75	497	3.0	2.66	796	1326
1978	9,905	4.17	430	0.75	573	3.2	2.91	1001	1668
1979	11,900	4.17	519	0.77	674	3.5	3.10	1289	2148
1980	14,120	4.17	599	0.80	749	3.7	3.09	1387	2312
1981	15,100	4.17	644	0.82	785	3.9	3.27	1515	2568
1982	16,460	4.17	714	0.85	840	4.1	3.68	1793	3092
1983	19,100	4.15	838	0.90	927	4.3	4.31	2280	4000
1984	23,400	4.10	1009	0.90	1121	4.4	4.43	2783	4970
1985	27,600	4.05	1195	0.88	1358	4.5	4.41	3290	5985
1986	33,850	4.00	1439	0.88	1635	4.6	4.47	4020	7310
1987	39,900	3.95	1682	0.86	1955	4.7	4.44	4684	8675
1988	48,000	3.90	1995	0.85	2348	4.8	4.50	5705	10566

Table 2-2 records the free-world polycrystalline silicon usage for the years 1977 to 1983. The table shows the industries that convert polycrystalline silicon to polished silicon wafers. Some companies such as Texas Instruments, Inc., Motorola Inc., and IBM manufacture polished wafers for internal use. Others such as Wacker, Monsanto, and Shin-Etsu Handotai manufacture wafers for sale. 1983 was a difficult time for all of these companies. During the first half of the year, sales were hard to generate; during the second half of the year, facility start-up problems had to be addressed to meet the rapidly increasing demand.

A forecast of free-world use of polycrystalline silicon through 1988 is presented in Table 2-3. The following wafering-related observations are implicit in this table:

- (1) No new company will become a major manufacturer of polished silicon wafers.
- (2) Merchant suppliers of polished silicon wafers will take over the business from the captive (device) manufacturers.
- (3) Four companies will be key wafer suppliers: Wacker, Monsanto, Shin-Etsu Handotai, and Osaka Titanium.

The complementary metal-oxide semiconductor (CMOS) technology will largely replace n-type metal-oxide semiconductor (NMOS) technology for the manufacture of silicon-integrated circuits during the next five years. This will require that polished-silicon wafer manufacturers add the epitaxy step to their processes and that they sell primarily epitaxial wafers rather than polished-silicon wafers. This change will entail some silicon feedstock losses in the epitaxial process, but will provide some gains in integrated-circuit yields. Overall, it is expected that these two factors will balance, and no net change in the use of polycrystalline silicon will occur due to this process step addition.

The world capacity for production of semiconductor-grade polycrystalline silicon for the years from 1977 to 1983 is presented in Table 2-4. The rated capacity shown in Table 2-4 and the actual production are two different sets of numbers. Polycrystalline silicon production and usage numbers also differ substantially. In the past, polycrystalline silicon refining plants frequently ran at capacity, and the product was either sold or stockpiled for future sales. In the future, this stockpiling practice will largely be discontinued because of the high-interest cost of inventory and the lower future market prices expected.

A world-capacity forecast of semiconductor-grade polycrystalline silicon production is made in Table 2-5. The projected growth rate of this capacity is impressive.

## B. REFINING INDUSTRY STATUS AND PLANS

The recent major changes in the semiconductor-grade silicon market sales, the technology improvement for silicon refining, and the prospect of increased market demand have forced important decisions and plans for the refining industry that are worth mentioning.



Table 2-2. Free-World Usage of Prime Semiconductor-Grade Polycrystalline Silicon, Metric Tons

Company	1977	1978	1979	1980	1981	1982	1983
1. Wacker Chemetronic GmbH	260	320	380	410	420	450	555
2. Monsanto Co.	260	320	380	410	420	440	525
3. Texas Instruments Inc.	130	150	190	200	210	230	240
4. Osaka Titanium Mfg. Co. <sup>a</sup>	100	130	200	210	215	360	620
5. Motorola Inc.	65	90	130	140	150	150	150
6. Shin-Etsu Handotai	60	100	160	180	250	450	750
7. Siltec Corp.	60	80	100	100	110	110	120
8. IBM	50	60	100	110	120	120	120
9. General Motors Corp.	60	70	80	80	85	90	100
10. Dynamit Nobel	40	60	80	90	110	200	220
11. Western Electric Co. Inc.	35	50	60	70	90	90	90
12. Fairchild C & I Co.	30	50	60	65	65	70	70
13. Komatsu Elect. Metals	30	40	50	50	75	100	170
14. Philips (Holland)	15	15	20	20	25	25	30
15. Ametek Inc.	-	-	-	10	10	10	10
16. Crysteco Inc.	10	10	10	10	20	20	25
17. Pennsilco	10	10	15	20	20	25	30
18. Cincinnati Milacron Inc.	-	-	-	5	15	20	30
19. Topsil (Denmark)	15	15	15	15	15	15	15
20. People's Republic of China	70	80	90	90	90	100	100
21. All Others	<u>26</u>	<u>18</u>	<u>26</u>	<u>27</u>	<u>23</u>	<u>17</u>	<u>19</u>
Annual Usage	1326	1668	2148	2312	2518	3092	3999

<sup>a</sup>Includes usage by Nihon Silicon and Toshiba Ceramics.

Table 2-3. A Forecast of Free-World Usage of Prime Semiconductor-Grade Polycrystalline Silicon, Metric Tons

Company	1984	1985	1986	1987	1988
1. Wacker Chemetronic GmbH	660	830	960	1220	1460
2. Monsanto Co.	630	780	940	1150	1300
3. Texas Instruments Inc.	290	300	300	300	300
4. Osaka Titanium Mfg. Co. <sup>a</sup>	800	1000	1200	1500	1800
5. Motorola Inc.	150	150	150	150	150
6. Shin-Etsu Handotai	1000	1200	1600	1800	2500
7. Siltec Corp.	190	270	300	340	380
8. IBM	120	120	120	120	120
9. General Motors Corp.	100	100	100	100	100
10. Dynamit Nobel	240	280	330	430	550
11. Western Electric Co. Inc.	100	100	100	100	100
12. Fairchild C & I Co.	70	70	70	70	70
13. Komatsu Elect. Metals	270	400	550	600	700
14. Philips (Holland)	30	30	30	30	30
15. Ametek Inc.	10	10	10	10	10
16. Crysteco Inc.	35	40	50	60	80
17. Pennsilco	40	50	60	80	100
18. Cincinnati Milacron Inc.	40	50	60	80	100
19. Topsil (Denmark)	15	15	15	15	15
20. People's Republic of China	130	135	240	400	550
21. All Others	<u>50</u>	<u>55</u>	<u>125</u>	<u>120</u>	<u>211</u>
Annual Usage	4970	5985	7310	8675	10566

<sup>a</sup>Includes usage by Nihon Silicon and Toshiba Ceramics.

Table 2-4. World Capacity to Manufacture Prime Semiconductor-Grade Polycrystalline Silicon, Metric Tons

Company	1977	1978	1979	1980	1981	1982	1983
1. Wacker Chemetronic GmbH	700	700	700	1200	1400	1800	2000
2. Hemlock Semiconductor Corp.	500	500	600	700	900	1000	1200
3. Osaka Titanium Mfg. Co. <sup>a</sup>	150	150	200	400	400	400	400
4. Texas Instruments Inc.	175	175	200	250	300	350	350
5. Dynamit Nobel	150	175	190	220	300	350	400
6. Monsanto Co.	175	190	200	210	230	230	230
7. Motorola Inc.	100	100	100	100	100	100	100
8. Great Western Silicon Corp.	-	10	50	100	200	200	200
9. Shin-Etsu Handotai	100	100	100	100	100	100	140
10. Komatsu Elect. Metals	30	30	30	60	60	60	60
11. Topsil (Pennsilco)	15	15	20	20	20	20	20
12. Union Carbide Corp.	-	-	-	-	-	10	54
13. People's Republic of China	100	100	150	200	200	200	200
14. USSR	<u>200</u>	<u>200</u>	<u>200</u>	<u>200</u>	<u>200</u>	<u>400</u>	<u>400</u>
Annual Capacity	2395	2445	2740	3760	4410	5250	5794

<sup>a</sup>Includes production of polycrystalline silicon by Hi Silicon Co.

Table 2-5. A Forecast of World Capacity to Manufacture Prime  
Semiconductor-Grade Polycrystalline Silicon, Metric Tons

Company	1984	1985	1986	1987	1988
1. Wacker Chemetronic GmbH	2000	2500	2500	2500	2500
2. Hemlock Semiconductor Corp.	1200	1200	1400	1500	1500
3. Osaka Titanium Mfg. Co. <sup>a</sup>	710	900	900	900	900
4. Texas Instruments Inc.	350	350	-	-	-
5. Dynamit Nobel	400	600	800	800	800
6. Monsanto Co.	230	230	-	-	-
7. Motorola Inc.	100	100		-	-
8. General Electric Co.	200	300	400	600	800
9. Shin-Etsu Handotai	140	140	-	-	-
10. Komatsu Elect. Metals	60	60	-	-	-
11. Topsil	20	20	20	20	20
12. Union Carbide Corp.	200	800	1200	2000	3000
13. Tokuyama Soda Co.	30	200	300	300	300
14. People's Republic of China	200	300	600	600	800
15. USSR & Satellites	300	400	600	800	1200
16. New Manufacturers	-	-	400	1000	1500
Annual Capacity	6140	7900	9120	11020	12820

<sup>a</sup>Includes production of polycrystalline silicon by Hi Silicon Co.

The planned shutdowns of the captive polycrystalline silicon plants at Motorola, Monsanto, and Texas Instruments have been postponed. Shutdowns at Motorola and Monsanto were planned because of production costs; the planned shutdown of the Texas Instruments plant was apparently based on silicon-purity issues.

The Wacker plant in Burghausen, West Germany, will continue to use the Siemens process with trichlorosilane to manufacture polycrystalline silicon. Wacker believes that the risks involved in the use of silane or dichlorosilane make it not worthwhile to convert the plant. Additional process changes will allow Wacker to increase the capacity of its Burghausen plant to at least 2500 metric tons. Wacker believes that fluidized-bed continuous-deposition technology using trichlorosilane (TCS) feedstock will not be on stream commercially until after 1990, and this will force other expansion decisions. Wacker improved the cost basis for the manufacture of polycrystalline silicon substantially during 1983 by installing a plant to recycle and hydrogenate the by-product silicon tetrachloride to TCS. With low-cost electrical power, on-site manufacture of TCS, and hydrogenation of by-product silicon tetrachloride, Wacker is today's lowest-cost producer of electronic-grade polycrystalline silicon.

Hemlock Semiconductor Corp. presently has an old, high-cost plant for the manufacture of polycrystalline silicon. The parent company, Dow Corning Corp., has been reluctant to invest large quantities of new money to renovate the plant. Shin-Etsu Handotai has recently purchased a 24-1/2% interest in Hemlock. Another 24-1/2% interest is likely to be sold in a joint venture arrangement. As a part of this joint venture, Hemlock is expected to make the necessary capital investments and add process improvements for the plant to become a low-cost producer. Among the changes expected are the recycling and hydrogenation of the process by-product silicon tetrachloride to TCS. The process changes have the potential to increase the capacity of the Hemlock plant and reduce production costs significantly.

The Japanese government has recognized that one of its huge industries is dependent upon imported polycrystalline silicon and has initiated efforts to produce low-cost silicon in Japan. The New Energy Development Organization (NEDO) has recently completed a TCS-manufacturing facility. This facility consists of a vertical fluidized-bed-type reaction tower filled with fine metallic silicon granules, into which silicon tetrachloride gas is blown from underneath to synthesize TCS. The Osaka Titanium factory has a production capacity of 200 tons/yr of TCS. It is also anticipated that Osaka Titanium, with joint ventures, will increase its polycrystalline silicon plant capacity to 800 metric tons in 1985 and to 1800 metric tons by 1990. Osaka Titanium has also conducted its own research to refine metallurgical-grade silicon to a product less pure than semiconductor grade. The patents granted indicate that a variant of the Siemens process will be used at Osaka Titanium with on-site silicon tetrachloride by-product recycling and hydrogenation.

NEDO also has developed an energy-efficient silicon refining process through a research and development project at Shin-Etsu Chemical Co., Ltd. In this process a fluidized bed is used to produce a solar-grade silicon continuously, and the unit power requirement (quantity of electricity required to produce 1 kg) is only about 30 kWh. This is much lower than the energy required

by the Siemens process and is similar to that projected for the Union Carbide Corp. silane process. In this new process, a mixture of gases consisting of TCS gas (four parts) and hydrogen (six parts) are blown up through a vertical fluidized bed, and solar-grade silicon seed crystals with particle diameters of 0.3 to 0.5 mm are dropped into the upper part of a fluidized bed that is maintained at a temperature of 1000°C to 1100°C. The seed crystals, upon coming into contact with the mixed gas, grow into larger, heavier crystals during transit through the fluidized bed and are collected continuously from the underside as large crystals with particle diameters of 0.8 to 3.0 mm. The hydrogen and silicon tetrachloride gases that rise to the upper part of the fluidized bed are recovered separately, with the recovered silicon tetrachloride gas recycled for hydrogenation and reuse as TCS feedstock. The experimental manufacturing facility installed in the Shin-Etsu plant has a solar-grade silicon production capacity of 10 tons/yr. It is also reported that, in the manufacturing facility's test run, the target unit energy requirement of about a tenth of the Siemens process was attained, but the product purity has not yet been established.

The Dynamit Nobel plant in Merano, Italy, uses the Siemens process with TCS feedstock to produce semiconductor-grade polycrystalline silicon. It is expected that this plant can be expanded to 800 metric tons by process changes. It has been reported that a new plant will be built when necessary as a joint venture with the Grace Chemical Co. or by Dynamit Nobel alone.

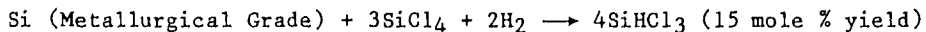
Motorola and Monsanto both operate Siemens-process plants that require purchased trichlorosilane. The plants are small in scale and high in operating cost. The current short-term limited availability of polycrystalline silicon has forced these companies to continue the operation of the plants. Both will probably shut down as soon as an adequate alternative supply of polycrystalline silicon is guaranteed.

General Electric Co. purchased the Great Western Silicon Corp. early in 1981. This plant uses purchased TCS in the Siemens process. GE had not increased the plant's capacity until recently. The plant will either be expanded to large capacity with on-site recycling or GE will cease operation of the plant.

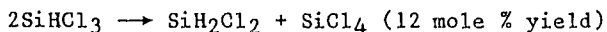
Shin-Etsu Handotai and Komatsu Electronic Metals both operate small, high-cost plants in Japan. Shin-Etsu Handotai will shut down its plant as soon as Hemlock can guarantee a sufficient supply of polycrystalline silicon. Komatsu plans to close its small plant as soon as UCC can guarantee a high-quality supply of polycrystalline silicon using the silane process.

The Topsil Silicon Materials Group in Denmark is an independent company manufacturing float-zone silicon crystal for advanced power devices. Topsil produces its own high-density polycrystalline silicon for the float-zone crystal. The company is expected to increase its capability as sales of their float-zone wafer products increase.

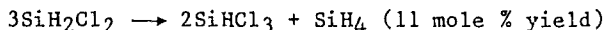
UCC developed, with the aid of DOE funding, an inexpensive method of converting metallurgical-grade silicon to silane. This process is detailed below:



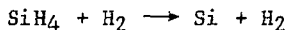
Conditions: Fluidized-bed reactor  
500°C, 515 lb/in.<sup>2</sup> actual  
CuCl catalyst



Conditions: Fixed-bed reactor  
80°C, atmospheric pressure  
Quarternary ammonium catalyst



Conditions: Fixed-bed reactor  
80°C, atmospheric pressure  
Quarternary ammonium catalyst



Conditions: 850°C, at atmospheric pressure

Technical expertise of the Komatsu Electronic Metals Co. has been licensed to decompose the silane thermally to semiconductor-grade polycrystalline silicon in a chemical vapor deposition reactor. A new plant with a capacity of 1200 metric tons per year using the Komatsu deposition reactor is expected to start production late in 1984. It is situated at Moses Lake, Washington. Activities for the designing and planning for an additional 3000-metric-ton capacity plant have also recently been announced; it will be installed in Washington in the late 1980s. Union Carbide is also conducting research on a fluidized-bed reactor jointly funded by DOE. Fluidized-bed reactors will be one of the options to decompose silane for the 3000-metric-ton plant.

The Tokuyama Soda Co. of Japan has licensed expertise from GE (Great Western). Tokuyama will essentially duplicate the GE plant in Japan.

The People's Republic of China has nine operating polycrystalline silicon plants. The largest is at Loyang, Hunan, and has an annual capacity of 25 metric tons. China is dissatisfied with all nine plants and is purchasing equipment to build a new, larger, and more cost-effective Siemens process plant.

Any trade in polycrystalline silicon between the free world and the USSR has essentially been stopped. Although the USSR seems to have sufficient polycrystalline silicon, it does not have the technology to convert it into high-quality integrated-circuit wafers.

The consortium of Allied Chemical Co., Eagle-Picher Industries, Inc., and General Atomic Co. built a laboratory-scale pilot plant to convert by-product  $\text{SiF}_4$  from the fertilizer industry to silane and to use a fluidized-bed reactor to decompose the silane to semiconductor-grade polycrystalline silicon. This small pilot plant was shut down and disassembled early in 1983. The technical expertise for this process is now for sale.

Three other laboratory-scale pilot plants in the United States use proprietary processes that could potentially manufacture low-cost, high-quality polycrystalline silicon. Two of these plants are based on silane and fluidized-bed decomposition. The third plant uses the hydrogen reduction of  $\text{SiHBr}_3$ . It is expected that at least two of these processes will go into production by 1988.

#### C. MARKET PRICING OUTLOOK

The market price of refined polycrystalline silicon depends on the supply-and-demand scenario, as with any other commodity. Nearly all of the material purchased is used by the semiconductor industry for the fabrication of integrated circuits, transistors, power diodes, and other electronic devices. The demand for photovoltaic devices has been very small, but is expected to increase steadily.

As much as 80% of all polycrystalline silicon is sold under long-term contracts that specify maximum and minimum yearly sales quantities that can or must be delivered or accepted. Such contracts can be broken only upon payment of specified penalties, and they specify yearly prices based on agreed-upon escalation scales. Few polycrystalline silicon producers would risk building a new plant without such signed contracts. Year-to-year silicon prices tend to be quite stable once a contract is in effect.

As much as 10% of all polycrystalline silicon is sold on the basis of one-year contracts under which the silicon is purchased in one year for delivery during the next year. During the past four years, silicon prices set on this basis have been far more volatile than those based on long-term contracts.

Less than 10% of all polycrystalline silicon sales take place on the spot market. Producers and long-term contractors take part as sellers in this market. During the past four years, prices on this market have been very volatile. For example, in July 1978, Smiel Co. sold 40 metric tons of prime semiconductor-grade polycrystalline silicon for \$40/kg. In July 1980, Great Western sold 30 metric tons of prime semiconductor-grade polycrystalline silicon for \$125/kg. In July 1982, Dynamit Nobel and Great Western each sold 30 metric tons of polycrystalline silicon for prices between \$38 and \$42/kg. Early in 1984 the spot-market prices jumped to about \$64/kg for short periods.

There are two types of "off-grade" polycrystalline silicon that are also sold on the spot market and tend to confuse the situation. This off-grade material, although not suitable for the most exacting uses such as manufacturing thyristors or random-access memories, is eminently suitable for use in the manufacture of solar cells, auto rectifiers, and as substrates for epitaxial



wafers. This material accounts for approximately 5% of all virgin polycrystalline silicon manufactured. It generally does not meet the specifications of prime-grade polycrystalline silicon because carbon, phosphorus, or boron levels are slightly too high. It is sold, as manufactured, to any interested buyer.

Silicon single-crystal Czochralski growth typically results in only 60% of the polycrystalline silicon feedstock emerging as sellable single-crystal wafers. The remaining silicon is scrapped or recycled. Most of this crystal scrap can be recycled and is suitable for regrowth into single-crystal material, which is then processed into wafers by the large crystal-growing companies for solar-cell manufacturers. Some of the crystal scrap is also made into wafers suitable for the manufacture of other semiconductor devices or is sold to solar-cell manufacturers as polycrystalline feedstock. The prevailing prices for the sale of this scrap in the past have varied between a quarter and half of the price of prime semiconductor-grade polycrystalline silicon.

Not all polycrystalline silicon reaches the market for sale as bulk polysilicon. Much of it is used by the manufacturers to produce wafers for sale. Table 2-6 gives a history of this wafer manufacturer usage of polycrystalline silicon. Table 2-7 predicts the growth of this internal use.

The semiconductor silicon weighted average selling price in previous years (current-year dollars) and the expected price in the future (1982 dollars) are plotted in Figure 2-1. It is forecast that the weighted average price in the future will decrease, based on these factors:

- (1) Adequate polycrystalline silicon supply is expected in the future, with the Siemens process improvements now being incorporated by industry. The capacity of the polycrystalline silicon manufacturers is growing faster than projected market demands.
- (2) Union Carbide and other U.S. manufacturing teams will enter the polycrystalline silicon market using new low-cost processes to produce a low-cost, high-quality product. These new entries can successfully enter the market only with prices lower than the competition or by offering a better product.
- (3) It is becoming evident that silicon-integrated circuits will be the electronic workhorse for the rest of this century. Such technologies as silicon on sapphire, Josephson junction devices, magnetic bubble memories, and gallium arsenide devices will have little effect on the silicon device market. Accordingly, polycrystalline silicon manufacturers are now convinced that the silicon market is here to stay and are willing to make the investments necessary to build the new and larger plants required for the future market.

At present the photovoltaic module manufacturers either buy polycrystalline silicon to grow and slice their own Czochralski wafers or buy silicon wafers directly. Scrapped-out polycrystalline silicon is now used primarily to fabricate solar cells. This trend will probably continue in the near future.

Table 2-6. Polycrystalline Silicon Used Internally by Manufacturers, Metric Tons

Company	1977	1978	1979	1980	1981	1982	1983
1. Wacker Chemetronic	240	310	370	390	400	400	570
2. Monsanto Co.	175	190	200	210	230	230	230
3. Osaka Titanium	100	126	190	220	280	300	300
4. Texas Instruments	120	150	180	180	1551	165	215
5. Motorola Inc.	75	90	100	100	90	90	100
6. Shin Etsu	90	100	100	100	100	100	100
7. Dynamit Nobel	30	50	80	90	115	180	200
8. Komatsu Electronic Metals	30	30	30	60	60	60	60
9. Topsil	15	15	15	15	15	15	15
10. People's Republic of China	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>	<u>90</u>
Totals	915	1111	1325	1435	1525	1620	1880

In the growth of silicon single crystals, approximately 60% of the polycrystalline silicon ends up as 'on spec' wafers. The remaining 40% is scrapped. The losses related to crystal growth are:

- (1) Crystal grinding, 3%.
- (2) Non-single-crystallinity, 2%.
- (3) High O<sub>2</sub> and carbon content, 3%.
- (4) Crucible tailings, 7%.
- (5) Crystal bottoms and tops, 10%.
- (6) Resistivity outside specifications, 15%.

The polycrystalline silicon left in the crucible after crystal growth and the grinding residue (items 1 and 4) are a true loss. The remaining losses (items 2, 3, 5, and 6) are, however, reclaimable for solar cells, diodes, and as substrates for epitaxial wafers. At least two-thirds of this scrap is available to the silicon solar-cell industry for inexpensive wafers or polycrystalline silicon.

Table 2-7. Projected Growth in Internal Use of Polycrystalline Silicon, Metric Tons

Company	1984	1985	1986	1987	1988
1. Wacker Chemetronic	660	830	960	1220	1400
2. Monsanto Co.	230	230	230	230	230
3. Osaka Titanium	300	360	460	640	800
4. Texas Instruments	270	350	440	450	600
5. Motorola Inc.	100	100	100	100	100
6. Shin Etsu	100	100	100	100	100
7. Dynamit Nobel	240	280	330	430	550
8. Komatsu Electronic Metals	60	60	60	-	-
9. Topsil	15	15	15	15	15
10. People's Republic of China	<u>140</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>400</u>
Totals	2215	2475	2995	3685	4195

Approximately 5% of all virgin polycrystalline silicon produced does not meet the specifications required for the manufacture of integrated circuits or power devices. The levels of phosphorus, boron, or carbon are critical for integrated circuits, but often less so for solar cells. This off-grade product is available to the solar industry for a price that is usually less than half the spot-market price for prime-grade polycrystalline silicon.

World photovoltaic shipment history and a forecast are given in Table 2-8 for silicon solar arrays. Japan is aggressively capturing an increasing market share, primarily because its industry excels in volume production of amorphous silicon solar cells, now used primarily for consumer products.

Silicon consumption history and a forecast for the manufacture of solar cells through 1988 are given in Table 2-9. Solar cells fabricated from Czochralski crystal and semiconductor-grade polycrystalline silicon usually have at least a 13% to 14% efficiency. This should increase to 14.5% to 15% by 1983 and 15% to 15.5% by 1985. Solar cells fabricated on polycrystalline ribbon have demonstrated efficiency near 15%. Single-crystal ribbon cells have shown efficiency higher than 16%. It is estimated that ribbons will be used to supply approximately half of the photovoltaic market beyond 1987. As can be seen in Table 2-9, the needs of the photovoltaic industry will exceed the

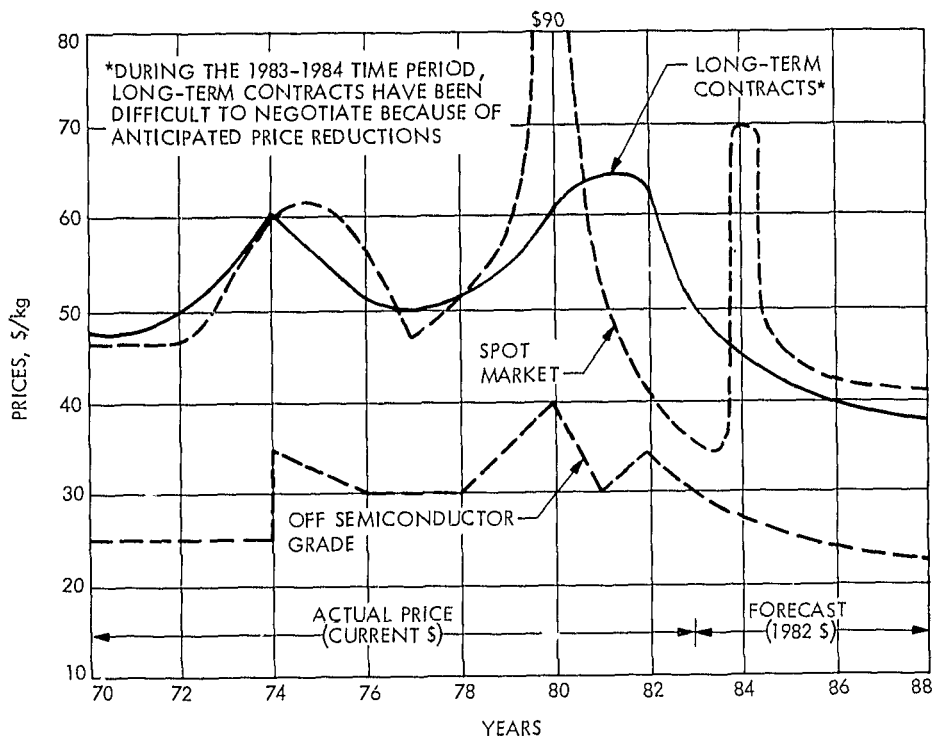


Figure 2-1. Weighted Average Price History and Forecast for Polycrystalline Silicon per Kilogram (1982 \$)

available volume of scrap-out polycrystalline silicon by 1987, and the photovoltaic industry will become a more significant user of prime polycrystalline silicon.

As a result of continuing wafer sawing research, slicing practices for ingots are expected to improve in the next few years. The slice thicknesses should decrease from 375 to 240 micrometers (0.015 to 0.010 in.) and the kerf loss from 300 to 240 micrometers (0.0121 to 0.010 in.). Crystal yields, even with continuous pulling, should average 75%, and crystal circumference grinding may be unnecessary. The amount of single-crystal ingot and polycrystalline silicon required to manufacture wafers for solar cells has been about 18 to 20 g/W, in the past. Using these assumptions, it is expected that silicon use will be reduced in the future to about 12 g/W by improved wafering techniques and higher cell efficiencies. With the ribbon technology, the polycrystalline silicon needed for manufacturing solar cells is expected to be near 6 g/W. Table 2-10 shows the weighted average price of semiconductor-industry scrap silicon that could be used by the photovoltaic industry to 1987, and a forecast of the price with the use of pure polycrystalline silicon beyond 1987.

Table 2-8. History and Forecast of Silicon Solar-Cell Array Shipment by Place of Origin, Megawatts

Place of Origin	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
United States <sup>a</sup>	1.1	2.0	2.4	2.5	3.5	4.9	12.5 <sup>b</sup>	16.0	28.0	50.0	100.0	200.0
Western Europe	0.2	0.3	0.3	0.4	0.9	1.7	3.3	3.5	4.5	6.0	10.0	25.0
Japan	0.0	0.1	0.3	0.5	1.1	1.7	5.3 <sup>c</sup>	8.0	12.0	20.0	80.0	160.0
Other	0.0	0.0	0.1	0.1	0.1	0.2	0.4	0.4	0.5	1.0	2.0	4.7
Totals	1.3	2.4	3.1	3.5	5.6	8.5	21.5	28.9	45.0	77.0	190.0	390.0

<sup>a</sup>Forecasts for U.S. shipments assume that photovoltaic tax credits will be extended at least through 1988.

<sup>b</sup>More than 4 MW of the shipments were concentrators that use 1% to 2% of the silicon material needed for an equivalent flat-plate power rating.

<sup>c</sup>Nearly 4 MW of Japan's 1983 shipments were small consumer-product power modules, mostly using amorphous silicon cells.

Table 2-9. Historical Use and Forecast of Polycrystalline Silicon Required for Silicon Solar-Cell Arrays

	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988
Average dollars <sup>a</sup> per peak watt	10.00	9.00	8.50	8.00	7.60	7.20	6.00	5.50	5.00	4.50	4.00	3.50
Solar cell modular ship- ments, peak megawatts	1.3	2.4	3.1	3.5	5.7	8.5	21.5	28.9	45	77	190	390
Polycrystalline <sup>b</sup> silicon required, metric tons	28	50	60	65	94	150	295	350	530	750	1700 <sup>c</sup>	3500 <sup>c</sup>
Scrap high-grade poly- crystalline silicon that could be used for PV, metric tons	225	280	250	400	425	470	550	675	830 <sup>d</sup>	1080 <sup>d</sup>	1360 <sup>d</sup>	1700 <sup>d</sup>

<sup>a</sup>Current year dollars; in 1984 and beyond, expected prices are in 1982 dollars.

<sup>b</sup>Assumes a small portion (20%) of the future solar array shipments consists of concentrators.

<sup>c</sup>Significant portion of PV need must be supplied from sources other than semiconductor device industry scrap.

<sup>d</sup>Estimates of scrap high-grade polycrystalline silicon available for PV may be high due to the recycling process the semiconductor device industry is planning to use.

Table 2-10. Weighted Average Prices of Off-Grade Polycrystalline Silicon, \$/kg

Year	Weighted Average Price	Year	Weighted Average Price
1974	35	1982	35
1975	32	1983	30
1976	30	1984	29 <sup>a,c</sup>
1977	30	1985	28 <sup>a,c</sup>
1978	30	1986	27 <sup>a,c</sup>
1979	35	1987	25 <sup>a,b,c</sup>
1980	40	1988	24 <sup>a,b,c</sup>
1981	30		

<sup>a</sup> Estimate.

<sup>b</sup> Includes the procurements of prime electronic-grade polycrystalline silicon.

<sup>c</sup> 1982 dollars.

### SECTION III

#### DEPARTMENT OF ENERGY SILICON REFINING PROCESS RESEARCH

In this section, the research conducted by FSA and the Solar Energy Research Institute (SERI) is reviewed. This research has been funded by DOE to develop the technology for refining processes capable of producing low-cost semiconductor-grade polycrystalline silicon. A probabilistic analysis of the potential for the UCC and Hemlock processes to achieve the National Photovoltaics Program cost goals is summarized, and the impacts of the Program upon the commercial polysilicon industry are discussed.

##### A. HISTORY OF THE SILICON REFINING RESEARCH TASK

The Low-Cost Solar Array Project (LSA), later renamed Flat-Plate Solar Array Project (FSA), was started by JPL in 1975 as a key effort in the U.S. solar energy research program. The goal of the project was to demonstrate the technology for low-cost terrestrial photovoltaic solar arrays. The project was originally sponsored by the Energy Research and Development Agency (ERDA) and is now funded by DOE. It was structured into several technical areas, each given a cost goal allocation to achieve the project goal of \$0.50/peak watt (1975 \$). The Silicon Material Task was assigned the responsibility for demonstrating the technology for low-cost polycrystalline silicon processes. The criteria were that the polysilicon must be suitable for fabricating photovoltaic solar cells meeting the project's energy conversion performance requirement and that the 1986 market price be <\$10/kg of silicon in 1975 dollars. The task plan had two major objectives:

- (1) To develop the technology for, and to establish the practicality of, processes capable of meeting the guidelines for production, energy use, and economics.
- (2) To develop information correlating the effects of impurities on photovoltaic cell performance, which could be used to define the purification requirements and the economics of the processes.

The plan was divided into phases as follows:

- (1) Determination of the technical feasibility of candidate processes by evaluating chemistry and chemical engineering data obtained from laboratory-scale experiments.
- (2) Evaluations of the potential practicality of the processes by analyses of data obtained in scaled-up reactors and of information from preliminary process design calculations.
- (3) Assessments of the performance characteristics of pilot-plant-scale Experimental Process System Development Units (EPSDUs) under simulated steady-state operation. The operational data were to form the basis for the final judgment of the capability of a



process to achieve the task goal and concurrently to provide information for the equipment and process designs for large production plants.

The SERI polycrystalline program objectives are to conduct research and studies of potential innovative refining processes for production of low-cost polycrystalline silicon.

The process developments and the primary studies of impurity effects were made at JPL under contracts with industry, universities, and non-profit institutes. Support in areas of chemical engineering, impurity effects, material and cell measurements, and economics was given in similar laboratories. Several consultants were used for analyses, critiques, and critical-problem reviews. The JPL staff conducted theoretical and experimental studies in JPL laboratories in the areas of material characterization and chemical reactor research. The staff also performed technical evaluations and managed the contracts.

Twelve polysilicon processes were investigated at JPL, most of them to an extent that technical evaluations of their potential to meet the task goal could be made. Developments were eliminated from the task program by decisions based on comparative technical evaluations when the task plan necessitated reductions in scope. In some cases, the potential economic and energy-use advantages of the eliminated processes were sufficiently encouraging that further development was continued under private funding. Examples are the bromosilane process of J.C. Schumacher Co., sodium reduction of silicon tetrachloride by the AeroChem Research Laboratories process, the direct-arc furnace process of Dow Corning Corp., and sodium reduction of silicon tetrafluoride by the SRI International, Inc. process. In each of these examples, chemical engineering studies to characterize the main reactor, to establish product purity, and to design a process remained uncompleted when the funding withdrawal decisions were made. The two processes that were the most extensively developed by the task were the Hemlock dichlorosilane (DCS) CVD process and the UCC silane process. A hydrochlorination reactor for converting metallurgical-grade silicon feedstock and recycled  $\text{SiCl}_4$  into  $\text{SiHCl}_3$ ; units for removing metals, and a redistribution reactor using an amine catalyst for converting  $\text{SiHCl}_3$  into  $\text{SiH}_2\text{Cl}_2$  are common to both processes.

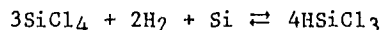
#### B. HEMLOCK SEMICONDUCTOR CORP. DICHLOROSILANE CHEMICAL VAPOR DEPOSITION PROCESS

The research and development of the Hemlock process was carried through the phase of the studies characterizing the operation of a process development unit for converting trichlorosilane into dichlorosilane at a rate of 100 kg/h. The conditions for the deposition in a modified stainless-steel chemical vapor deposition reactor (with cooled walls) were to be established, meeting the contract goals of a rate of 2 g/h per cm rod length and 40% conversion yield. The goal for energy use of 60 kWh/kg was not attained, the average experimental value being 90 kWh/kg. The product was shown to be equivalent to semiconductor-grade silicon. However, the data developed, which describe the flammability and explosive properties of DCS, showed it to be far

more hazardous than TCS or hydrogen. This concern forced a redesign of the process so that no DCS storage is allowed. The DCS ( $\text{SiH}_2\text{Cl}_2$ ) is diluted with hydrogen directly after distillation and then is fed into the deposition reactors. The decision for the commercialization of this process based on the Hemlock process flow diagram shown in Figure 3-1 (Reference 8) will depend on trade-offs involving the advantages of conversion yield, deposition rate, energy use, and the disadvantage of operating without a DCS storage tank.

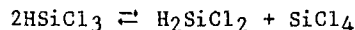
The chemistry involved in the DCS CVD process is well established, as is the reactor technology. The stoichiometric equations are given here. The deposition reaction yields are approximately 15%  $\text{HSiCl}_3$ , 12%  $\text{H}_2\text{SiCl}_2$  and 40% Si.

Hydrogenation of Metallurgical-Grade Silicon and Silicon Tetrachloride:

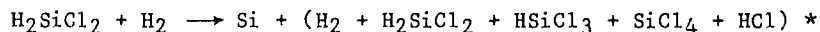


Dichlorosilane Synthesis:

Catalyst



Dichlorosilane Decomposition:



#### C. UNION CARBIDE CORP. SILANE PROCESS

The DOE-JPL-sponsored research and development of the silane process by UCC was structured in three phases. In Phase I, the engineering feasibility of the process was proven by determining the conditions for silane ( $\text{SiH}_4$ ) production from  $\text{mgSi}$  in a small-scale process development unit and by showing that the free-space reactor and the fluidized-bed reactor were both candidates for the silicon deposition step. A complete process flow sheet was developed from engineering process design studies. Then, in Phase II, a detailed process design package was completed for a 100-metric-ton/year Experimental Process System Development Unit (EPDSU). Phase III was for the design, installation, operation, and evaluation of the EPDSU and for the continued development of a continuous deposition reactor for low-cost, large-scale production.

The silane process is a two-stage process. Reaction steps for the conversion of  $\text{mgSi}$  and recycled silicon tetrachloride ( $\text{SiCl}_4$ ) and  $\text{H}_2$  into  $\text{SiHCl}_3$  (TCS) and then the sequential redistribution of  $\text{SiHCl}_3$  into  $\text{SiH}_2\text{Cl}_2$  (DCS) and  $\text{SiH}_4$  are in the first stage. The thermal decomposition

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\*Qualitative equation only; exact reaction is temperature and composition dependent.

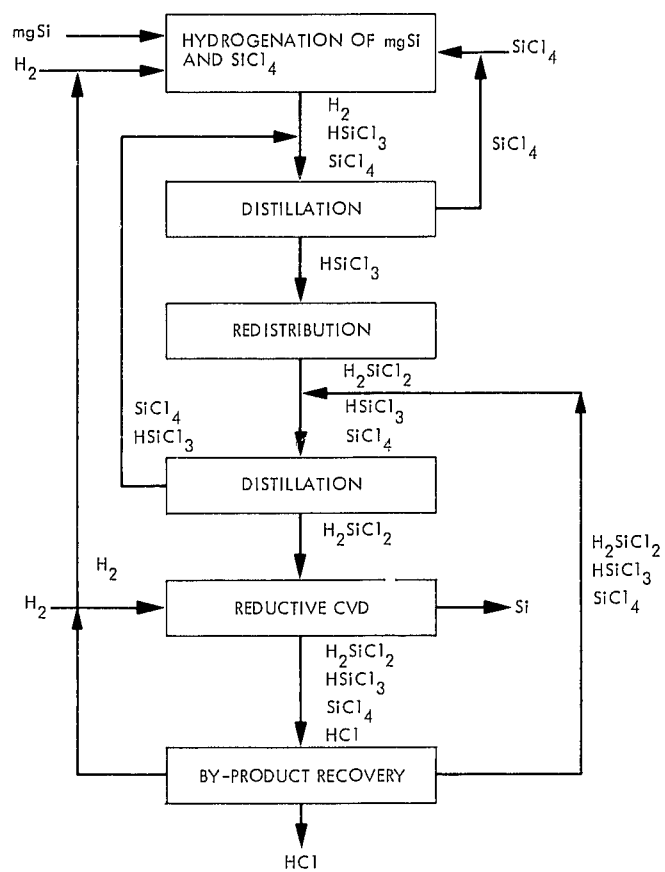


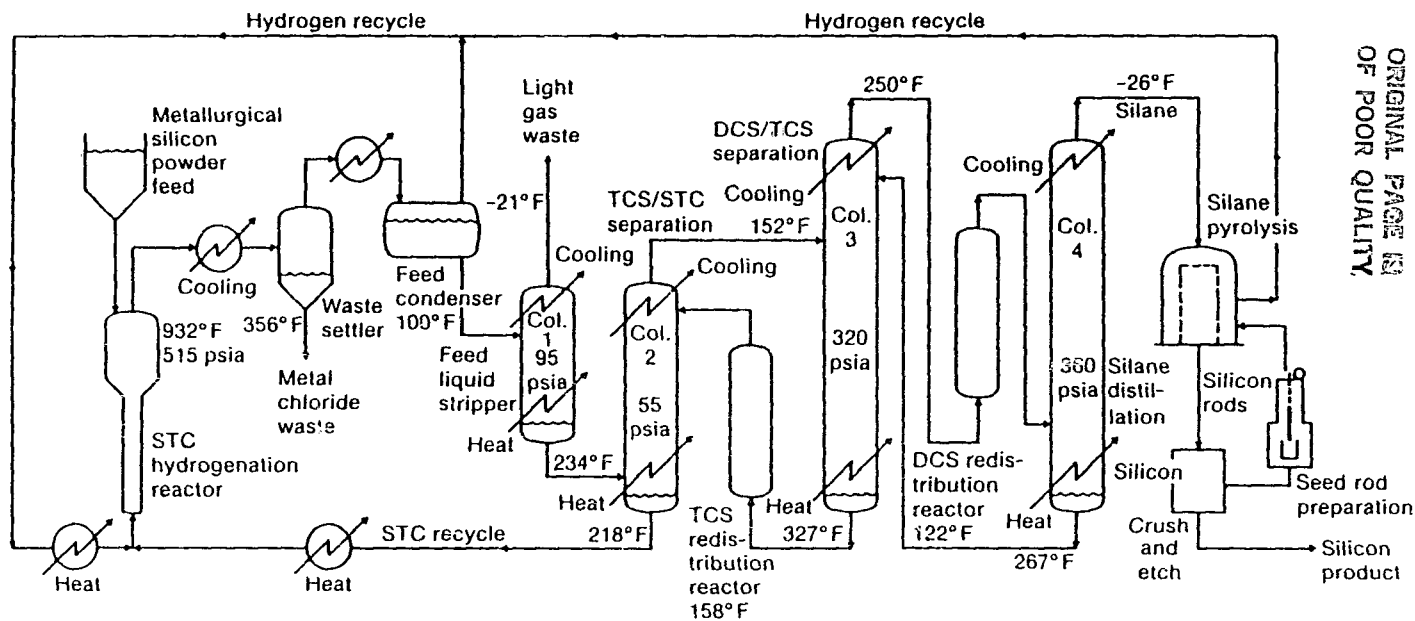
Figure 3-1. Flow Diagram of Hemlock Semiconductor Corp. Dichlorosilane-Based CVD Process

of the  $\text{SiH}_4$  into Si takes place in the second stage. The  $\text{H}_2$  and  $\text{SiCl}_4$  reaction by-products are efficiently recycled back to the hydrochlorination reactor to be used in the formation of the  $\text{SiHCl}_3$ . Reaction data to optimize the hydrochlorination reactor were also obtained by J. Mui at the Massachusetts Institute of Technology and Solarelectronics Corp. Some  $\text{SiCl}_4$  is added to provide make-up chlorine for the amount removed in the impurity metal chlorides during a front-end purification step. The  $\text{SiH}_4$  distillation column is designed to remove diborane, the contaminant most difficult to eliminate, to a concentration of less than 10 parts per trillion atomic. The thermal conversion of  $\text{SiH}_4$  to silicon in the EPSDU is being carried out in a CVD reactor; fluidized-bed technology is being developed to provide the advantages of low energy use and high throughput. The overall yield of very pure silicon is about 85% of the mgSi feedstock supplied to the process.

The installation of the EPSDU was begun in East Chicago, Indiana, but completion became impossible in mid-1981 due to severe budget reductions. To complete the EPSDU demonstration of the low-cost production capabilities of the  $\text{SiH}_4$  section of the process, the UCC contract was modified, requiring an obligation by UCC to complete the installation, to operate the EPSDU experimentally for the determination of steady-state conditions, to obtain data for redesign and optimization, and to supply JPL with all of the design and operation data for the silane section in return for transferring the title of the EPSDU equipment to UCC. The data for the proprietary CVD reactor (Komatsu Electronics Ltd.) will not be given to JPL under the agreement. Accordingly, the EPSDU was dismantled and reinstalled at a UCC site in Washougal, Washington. Although a number of design changes have been made and several pieces of equipment have been replaced during the experimental operation of the EPSDU, the performance has been brought up to designed levels. The product from the CVD reactors is of the highest purity; for example, resistivity of 26,000 ohm-cm, which is significantly better than semiconductor-grade specifications.

A detail of the silane process is shown in Figure 3-2. In the first reactor, mgSi of an average diameter of 300 micrometers is fluidized by the gas reactants, hydrogen and silicon tetrachloride ( $\text{SiCl}_4$ , or STC). A copper catalyst may be added. The reactor is operated at  $510^\circ\text{C}$  and 500 lb/in.<sup>2</sup> with the stream of equimolar, recycled gases being preheated. The product stream contains about 15% TCS, 44%  $\text{H}_2$ , and 41% STC, along with some Si dust and metal chloride contaminants. The mixture is quenched and moved into a settler tank where the insoluble metal compounds are removed. At this point the  $\text{H}_2$  is removed and recycled to the hydrogenation reactor; the by-product  $\text{H}_2$  from the deposition reactor is also recycled to the hydrogenation reactor. The crude TCS/STC mixture is moved to a storage tank. This mixture is first fed to a stripper column to remove the contaminant gases lighter than  $\text{SiH}_4$  to at least 0.01 parts per billion and 99% of the heavy contaminants. The reactant mixture is then fed to the second distillation column along with the recycle stream from the first redistribution reactors. This column is designed to separate 97% of the TCS overhead and to reject 97% of the STC as the bottom liquid.

The trace metal contaminants,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{CaCl}_2$ , have a higher boiling point than the TCS and thus will be rejected with the STC and eventually removed as sludge from the settler tank. If any of these metals are present as hydrides, they will still be with the TCS.

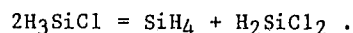
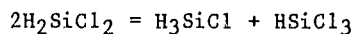
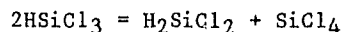


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Source: Final Report, Low-Cost Solar Array Project, Contract No. 954334, Union Carbide Corp.

Figure 3-2. Flow Schematic of the Union Carbide Corp. Ultra-High-Purity Silicon Process

The TCS, which also has monochlorosilane and DCS mixed with it, is fed into the third column, along with a second feed from the recycle of the silane column. This is set to deliver 97% of the TCS to the bottom and 97% of the DCS to the top as distillate. The bottom product is cooled and fed through a Rohm and Haas Amberlyst A-21 amine-base ion exchange resin in the first catalytic redistribution reactor. This reactor catalyzes the following reactions:



The predominant product is DCS, the yield being about 12%. The product stream from this redistribution reactor is fed to the third column to separate the DCS from the STC, which is recycled.

The DCS is fed into a second redistribution reactor containing the same catalyst to produce about 11 mole %  $\text{SiH}_4$ . The product stream is fed into the fourth column, which is designed to remove  $\text{B}_2\text{H}_6$  to <0.010 parts per billion and thus to yield very pure  $\text{SiH}_4$ . The  $\text{SiH}_4$  is stored as a liquid and fed as a gas to the deposition reactors. The TCS mixture from the final column is returned to the third distillation column.

#### D. SILANE-TO-SILICON CONVERSION PROCESS

The research for the development of a fluidized-bed reactor (FBR) for silane ( $\text{SiH}_4$ ) decomposition is being conducted by both JPL and UCC. The primary objectives of the JPL research are to characterize silicon deposition at high  $\text{SiH}_4$  concentrations, to develop a means for seeding the bed, and to determine the required fluidized-bed operating conditions to produce semiconductor-grade silicon. The UCC program is focused on establishing the conditions for steady-state operation at a  $\text{SiH}_4$  concentration of about 25% and for ensuring semiconductor-grade product purity. Considerable progress has been made in both programs. At JPL the reactor characteristics have been studied using  $\text{SiH}_4$  concentrations of 20% through 100%. The operational conditions have been adjusted so that greater than 90% silicon deposition in the bed has been obtained, even at the highest silicon concentrations. Good deposition rates occurred; in the run at 80%  $\text{SiH}_4$ , the deposition rate was 3.5 kg/h. At UCC, operation was maintained continuously for 44 h using a 20%  $\text{SiH}_4$  concentration. However, unacceptable contamination of the product has occurred in both reactors due to silicon particle abrasion of the metallic reactor walls. Liners of quartz and silicon will be inserted in the reactors to prevent contamination in future runs. The full establishment of the silane process as a low-cost polysilicon process meeting the FSA economic goal depends on the completion of the development of the fluidized-bed deposition technology.

#### E. NEW POLYSILICON REFINING PROCESSES

JPL has a contract with Energy Materials Corp. for the development of an electrochemical silicon refining process that uses mgSi feedstock: solar-grade silicon is deposited on a graphite cathode from a  $\text{Cu}_3\text{Si}:\text{Si}$  anode by electrolysis in a molten-salt cell. The silicon-copper alloy and the electrolyte are contained in a vitreous carbon crucible at temperatures of  $750^\circ\text{C}$  to  $800^\circ\text{C}$ . The alloy is formed from  $\text{mgSi}$  and 99.999% pure Cu containing 1 ppm Fe as the majority impurity. The electrolyte is a molten mixture of Suprapur\* lithium fluoride and Suprapur potassium fluoride with  $\text{K}_2\text{SiF}_6$  added as the transport agent. The  $\text{K}_2\text{SiF}_6$  is synthesized in situ by reactively dissolving high-purity  $\text{SiF}_4$  in a KF-rich melt. At operating temperatures, the silicon-copper alloy is a two-phase solid with a primary silicon phase embedded in a  $\text{Cu}_3\text{Si}$  matrix. This facilitates the casting of silicon plates, a prerequisite for an efficient, low-cost electro-refining process. The use of this composite as an anode enhances the purity of the refined silicon by about two orders of magnitude. This enhancement is due to the semipermeable nature of the  $\text{Cu}_3\text{Si}$  phase. This process was originally researched at SERI and has been shown to be an efficient and potentially cost-effective process for producing solar-grade silicon.

SERI is investigating the refinement of mgSi by a chemical vapor transport filtration (VTF) process. In this process, a  $\text{Cu}_3\text{Si}:\text{Si}$  anode reacts with hydrochloric acid (HCl) vapor to produce chlorosilanes which are then decomposed on hot silicon filaments to produce silicon. The silicon transport rate in this process has been measured and the results support the hypothesis that the transport may be limited by diffusion rate of the silicon in the anode. Experiments are under way to determine the activation energy. A large ref., which permits the use of considerably larger anodes, is planned.

A single-crystal silicon boule with (111) orientation was grown from 75 kg of VTF silicon material using a Czochralski crystal-growth technique. Devices made from this crystal measured a total area ( $0.1 \text{ cm}^2$ ) efficiency of 9.8%. The control cells had an average efficiency of 9.6%, with no cell having  $V_{oc}$  greater than 604 mV. These results indicate that the VTF-refined silicon is of good quality for solar-cell applications.

#### F. PROBABILISTIC ANALYSIS OF SILICON COST FOR UNION CARBIDE CORP. AND HEMLOCK SEMICONDUCTOR CORP. PROCESSES

A probabilistic analysis (Reference 10) was performed at JPL, using the SIMRAND (Simulation of Research and Development) model and the Improved Price Estimation Guidelines (IPEG) methodology, both developed by JPL. SIMRAND is a Monte Carlo simulation model that can perform algebraic operations on probabilistic inputs. This analysis assessed the probability that the new refining processes can achieve the current DOE cost targets of less than \$20/kg with a goal of \$16/kg (1982 \$).

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\*Trade name of Merck Co., Germany, for fluoride chemicals.

The IPEG methodology was used to provide cost estimates for manufacturing facilities. The IPEG results using identical inputs were compared with the data from the cost analyses performed by Lamar University and the Texas Research Engineering Institute to verify this methodology for a chemical processing plant. On the average, the differences were about 2.6%.

The IPEG equation includes inputs for plant investment, equipment costs, materials costs, utilities costs, labor costs, and output quantity. For this study, a reference output capacity of 1000 metric tons per year was chosen for use throughout the analysis.

This cost-estimating methodology was then incorporated into the probabilistic analysis. Probabilistic distributions were used as inputs to the IPEG equation. In the case of equipment cost, the processes were separated into sections and distributions were encoded for each one. Each section represented a step in the silicon purification process. Similarly, utilities cost was encoded by type (i.e., electricity, steam, etc.). These were aggregated to produce the input. For materials costs and labor costs, the total input for the process was encoded directly because breakdown by process step was more difficult. This strategy captured the essence of the economics of the processes while keeping the data encoding and analysis task workable. Items such as recycle loops were not modeled separately, but their influence on plant economics can be seen through their impacts on other inputs.

A distribution for each variable was initially encoded based on data from experts within JPL. In a second encoding round, the data were refined and inputs were included from the companies developing the processes. For those cases where the inputs of industry and JPL differed, a compromise distribution was developed. For some variables, proprietary restrictions forced the industry representatives to limit their inputs to brief comments on the JPL distributions. Seventeen of these distributions were encoded using this methodology. These data formed the basis for the remainder of the analysis.

To perform arithmetical operations using probabilistic inputs in a practical manner, the SIMRAND model was used. The Monte Carlo simulation model can include equations and perform the necessary operations using probabilistic inputs.

Some economic assumptions had to be made to perform this analysis. The assumptions were: an equipment lifetime of 10 years; income taxes and property taxes of 50% and 2%, respectively; business investment tax credits, rate of return on equity of 20%; and contingencies of 15% of the total equipment cost. The remaining assumptions are numerous, but do not have a large effect on the results.

Figure 3-3 shows the results of the analysis. The three cumulative probability curves of price per kilogram of silicon represent the range of price expected for the UCC silane processes (using the FBR and Komatsu reactor as labeled) and the Hemlock process. The curves extend, from lower left to upper right, from the most optimistic to the most pessimistic scenarios for each technology. The vertical axis represents cumulative probability from 0% to 100%. A point on the curve portrays the probability that the technology



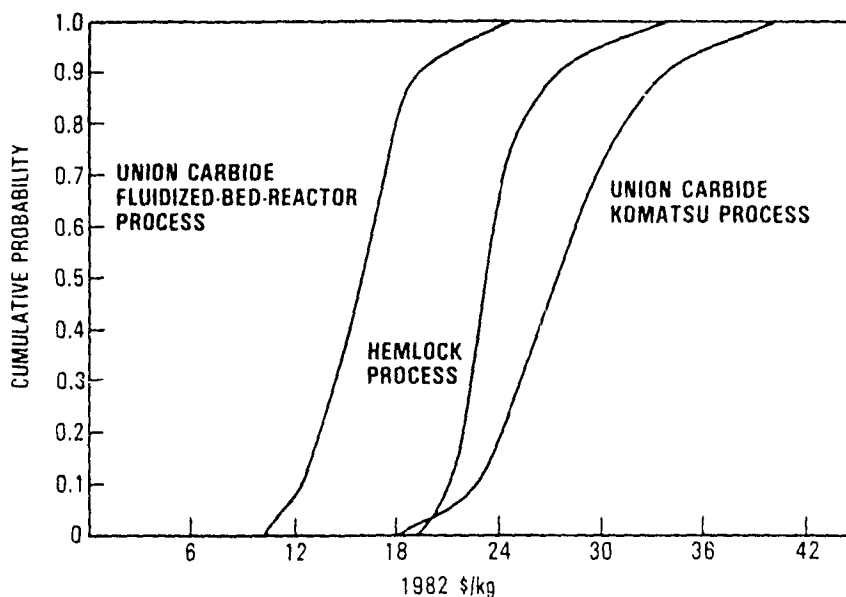


Figure 3-3. Cumulative Probability Distribution for Silicon Cost for Three Refinement Processes

will be capable of producing silicon at less than or equal to that cost. (See Reference 10 for the sensitivity factors and key parametric drivers that influence the results.)

The prospects for reaching the DOE cost goal look promising for the UCC FBR process. There is greater than a 90% chance that the product cost from the FBR process will be less than \$20/kg (1982 \$). There is a 55% chance of meeting the \$16/kg (1982 \$) cost allocation target price with this technology. This target price is equivalent to the original PV program allocation of \$10/kg (1975 \$).

The UCC Komatsu process and the Hemlock process both show a lesser chance of being very low in cost. The results show a 10% and 5% chance of producing silicon at \$20/kg (1982 \$) or less for the Hemlock and UCC processes, respectively. The Hemlock process, however, does show a greater than 90% chance of producing silicon at \$27/kg (1982 \$) or less. For the UCC-Komatsu process, the 90% level is \$34/kg (1982 \$). These data are not as firm as for the Hemlock process, as only minimal information is available concerning the Komatsu deposition reactor. This is shown in Figure 3-3 by the relatively shallow slope of the probability curve for the UCC-Komatsu process.

It should be noted that the costs developed by this analysis are technologically feasible production costs and do not predict actual market selling prices. Market selling prices will be determined by market conditions, corporate pricing strategies, and other factors beyond the scope of this discussion.

## G. IMPACTS AND PROSPECTS FOR COMMERCIAL POLYSILICON PRODUCTION

The results obtained by the FSA Silicon Material Task for the development of low-cost polysilicon processes can be most clearly associated with the commitments of UCC to use the silane process in large-scale production plants. As noted above, a pilot plant of about a 125-metric-tons-per-year capacity is on stream in Washougal, Washington. In addition, the construction of a 1200 metric-ton-per-year plant in Moses Lake, Washington, is under way with completion scheduled for later in 1984; in the latter case, the plant design allows for doubling the capacity in the future. Union Carbide has also announced (in February 1984) that the design and planning for a 3000-MT/year plant are being carried out. The Komatsu CVD reactors of proven capability may be installed at the large plants. The decision of whether to install FBRs will depend upon the timely availability of a demonstrated engineering design. The attributes of low energy use and high throughput would favor the use of FBRs for low-cost large-scale production, provided that purity and material form are acceptable to the users.

Successes at various steps in the development of the silane process have inspired other companies to make chemical engineering analyses and to conduct experimental programs in the preparation and use of  $\text{SiH}_4$  for polysilicon production. Some of these activities have dealt with the production of  $\text{SiH}_4$ , and others with the conversion of  $\text{SiH}_4$  to Si. For example, the Allied Corp. has described its process for producing  $\text{SiH}_4$  in a patent and apparently solicits cooperative ventures for polysilicon plants. Other industrial laboratories are developing alternative approaches for preparing silane. The development of FBR technology is also being done by industry. These endeavors are proprietary and there is a lack of published data or reports for comparing any of them with the well described and documented technology developed by JPL and by UCC under contract with FSA. Completion of the ongoing FBR research would result in a refining process that would be extremely advantageous to the industry.

The hydrogenation reactor of the silane process provides the capability of introducing mgSi for conversion to TCS while converting recycled STC to TCS. Its utility is extendable to all polysilicon processes that use TCS as an intermediate or as a reactant for Si deposition. Thus, it is adaptable for incorporation into the TCS Siemens process, the TCS FBR process, and the DCS-Siemens process.

The JPL-Schumacher process has attracted investors to sponsor a larger pilot plant that uses silicon tribromides as a raw material. At least three other companies are evaluating silane as a feedstock for polysilicon deposition. With large quantities of pure silane becoming available as a result of UCC's commercial activities, other semiconductor silane producers have improved their products. Thus, the semiconductor device industry and amorphous-silicon photovoltaic research, which both depend on silane, have been enhanced.

Studies of the effects of impurities on the performance of photovoltaic cells, which were intended to be used to define the purification requirements of polysilicon refining processes, also provided information for the selection of the conditions for the processing sequence for converting polysilicon into cells. Thus, the data on the interrelationships of impurity

content and process steps can be used for calculations of the functional sensitivity of cell behavior to these factors. These relationships can, in turn, be used for the determination of the requirements for the polysilicon composition and the appropriate processing procedures for defined cell specifications. Extensive experimental data were obtained and the effects of impurities, process steps, and impurity process integration were described by equations. Extensive contract effort was made by the Westinghouse Research Center under the direction of R. Hopkins (the contributions of the late R. Davis as a principal investigator in the theoretical analysis and in structuring the studies were especially notable). The data and correlations were used by A. Yamakawa of JPL (Reference 11) to devise a slide rule to identify the effects of impurities on solar-cell efficiency, taking into account various procedures for converting the polysilicon into simple crystalline ingots or ribbons. This experimental information and the theoretical investigations done by Professor C.T. Sah, under JPL contract, relating the effects of impurity content and cell design on cell characteristics, have formed the basis for the research program to develop high-efficiency cells.

Another benefit from the impurities studies is the development of the requirements for a solar-grade polysilicon material with specific impurity levels that would be acceptable to produce a desired solar-cell efficiency. The specification for the solar-grade polysilicon would be different from the present commercial semiconductor-grade silicon. Based on specific impurity levels of the solar-grade material, solar cells can be produced having a desired efficiency. For the highest possible solar cell efficiency, this solar-grade polysilicon may have impurity requirements that are even more stringent than those specified for the present commercial semiconductor-grade silicon.

Research funded by DOE has been instrumental in developing a number of technically feasible low-cost silicon refining processes that are now used or are expected to be used by the commercial refining industry. The achievements, which can be attributed directly to National Photovoltaics Program research, have resulted in or will result in many millions of dollars of cost savings to the commercial refining industry for the production of semiconductor-grade polycrystalline silicon.

In summary, the key DOE-JPL silicon refining research and development achievements are:

- (1) A process step for preparation of trichlorosilane using metallurgical-grade silicon, recycled hydrogen, and silicon tetrachloride.
- (2) A process for the production of low-cost, very pure silane.
- (3) An integrated silane process for the production of very pure silicon.
- (4) An integrated dichlorosilane chemical vapor deposition process for the production of semiconductor-grade silicon.
- (5) The basic fluidized-bed technology steps for the silane to low-cost silicon deposition.

## SECTION IV

### SUMMARY AND CONCLUSIONS

Over the past five years the JPL Photovoltaics Program PA&I Center has conducted silicon refining industry surveys to establish the current and future availability of refined silicon and the product market price the photovoltaics industry is and will likely be paying for the fabrication of solar cells.

Another objective of these surveys was to assess the plans of the silicon refining industry and industry reactions to the technology developments funded by DOE to provide low-cost polycrystalline silicon for the photovoltaics industry. The surveys were conducted primarily by Remo Pellin, a JPL consultant.

Many industry contacts have been established in these surveys and the industry has been cooperative, friendly, and very active in keeping up with state-of-the-art development activities to improve the quality of the semiconductor-grade silicon produced, to increase yield, and to reduce cost.

Although some of the data presented in this report indicate that plant capacity is in excess of demand, the industry has closely matched production to market demands. There were, however, some periods during which polysilicon for spot-market purchases was in short supply and, as a consequence, spot-market selling prices skyrocketed.

The years 1980 through most of 1983 were low sales years for polycrystalline silicon. The late-1983 boom in sales caught all producers by surprise and, early in 1984, annual production was not up to demand. In this period, polished-wafer companies were taking steps to increase production substantially. Normally these companies recycle about 10% of the scrap polycrystalline silicon back into their processes. Because this practice reduces polished-wafer yields somewhat, it has been minimized for the present. Eventually all scrap silicon may be used for recycling at the crystal-growth stage. The discontinuance of scrap recycling factor has increased near-term polycrystalline silicon wafering supply requirements by 10%. All polished-wafer users are more optimistic about their business now but are concerned about a possible near-term polycrystalline silicon shortage. On the average, most companies are ordering 10% more polycrystalline silicon than is required for day-to-day needs in order to increase inventory.

The use rate of polycrystalline silicon in early 1984 was at least 20% higher than expected. In early 1984, the world polycrystalline silicon production rate was about 4000 metric tons per year, and based on a forecast demand of 3960 metric tons for 1984, it can be assumed that sporadic short-term shortages may develop. Because Wacker Chemetronic GmbH and Hemlock Semiconductor Corp. will increase capacity by process changes and Union Carbide Corp. will come on stream late in 1984 with a new plant, polished-wafer manufacturers will come to accept, temporarily, shorter inventories and will use some scrapped-out polycrystalline silicon. Thus enough polycrystalline silicon should be available for all, although some transient conditions of limited spot-market supply may persist.

Today and in the near future, most polycrystalline silicon will be manufactured by Siemens- and modified-Siemens-process plants. Wacker and Osaka Titanium Mfg. Co. will use trichlorosilane as the silicon-source ingredient. Hemlock uses trichlorosilane now and may eventually use dichlorosilane. UCC will use silane for production of silicon.

Research and development projects sponsored by DOE and managed by JPL have developed improved processes and procedures for producing lower-cost polycrystalline silicon manufactured by variants of the Siemens process. Research sponsored by DOE/JPL and performed by UCC and Solarelectronics, Inc. on the hydrogenation of silicon tetrachloride to trichlorosilane has now been applied to full production at Wacker and soon will be at Hemlock and Osaka Titanium. This research showed how by-product silicon tetrachloride could be reduced inexpensively to trichlorosilane in the presence of metallurgical-grade silicon. The process is shown as Reaction 2 in Figure 2-1. The process modification at Wacker apparently reduced the manufacturing cost of polycrystalline silicon from over \$30/kg to about \$24/kg. It is expected that this process step will be used by all polycrystalline silicon manufacturers for the rest of this century, regardless of the exact process definition.

The Hemlock polycrystalline silicon plant might have been forced to shut down if JPL-sponsored research had not shown a way to continue potential profitability, by modernizing with new process steps such as hydrogenation of silicon tetrachloride to trichlorosilane. With this change, Hemlock should be able to produce polycrystalline silicon at a cost competitive with Wacker's, despite disadvantageous electric utility and labor costs.

Perhaps the most classic example of Government-sponsored high-risk research, showing a promising result and involving industry commercialization of the process, is the UCC process. UCC had considered entering the polysilicon business several times before 1980, but did not make the commitment until the JPL program showed technical feasibility. With a 120-metric-ton polysilicon plant in operation, a 1200-metric-ton plant scheduled to start up late in 1984, and a 3000-metric-ton plant announced for 1988, UCC will help make the United States a dominant force in world production of refined silicon. The new UCC Moses Lake, Washington, plant will require an investment of \$100/kg of annual capacity. The great majority of this investment is in Komatsu reactors for the final decomposition step. Thus, even plants with an annual capacity of 1200 or 3000 metric tons are expensive. The fluidized-bed deposition reactor, if successful, should greatly reduce the capital cost when installed in future silicon refining plants.

DOE-funded research has been instrumental in developing a number of technical achievements and integrated approaches for low-cost refining processes that are or are expected to be used by the commercial refining industry. Achievements that can be directly attributed to the PV program research have or will result in many millions of dollars of cost savings to the commercial refining industry for the production of semiconductor-grade polycrystalline silicon.

It can be said that the overall DOE-sponsored silicon materials research program has had a major effect on both the world's polysilicon producers and silicon supply. It is one area in which the United States, through proper use of Government funds, has maintained technology leadership.

## SECTION V

### REFERENCES

1. Costogue, E., et al, Silicon Material Outlook Study for 1980-1985, JPL Publication 79-110, Jet Propulsion Laboratory, Pasadena, California, November 1, 1979.
2. Costogue, E., et al, Industry Survey Report Status of Silicon Material and Silicon Sheet Techniques, JPL Internal Document No. 5230-5, Jet Propulsion Laboratory, Pasadena, California, May 1, 1981.
3. Snyderman, N., Electronic News, October 20, 1980.
4. Costogue, E., Polycrystalline Silicon Material Availability and Market Pricing Outlook Study for 1980 to 1988, JPL Internal Document No. 5230-10, Jet Propulsion Laboratory, Pasadena, California, February 1983.
5. Bary Toronto, Electronic News, February 27, 1984.
6. Mehler, M., Electronic News, February 20, 1984.
7. Mehler, M., Electronic News, October 3, 1983.
8. Final Report, JPL Contract 955533, Development of a Polysilicon Process Based on Chemical Vapor Deposition, Hemlock Semiconductor Corp., June 25, 1982.
9. Lorenz, J.H., A Survey of the Preparation, Purity, and Availability of Silanes, Subcontract Report, Solar Energy Research Institute, Golden, Colorado, December 1983.
10. Reiter, L.J., A Probabilistic Analysis of Silicon Cost, Jet Propulsion Laboratory, JPL Document No. 5101-246, JPL Publication 83-94, Pasadena, California, November 15, 1983.
11. Yamakawa, A., The Effects of Impurities on the Performance of Silicon Solar Cells, JPL Publication 5101-189, Jet Propulsion Laboratory, Pasadena, California, September 1, 1981.