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PROCESSES AND PROCESS DEVELOPMENTS IN JAPAN

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MOVE TO DEVLOPMENT OF LOW-COST POLYSILICON IN JAPAN

The commercialization of solar power generation necessitates the development of a new, low-cost manufacturing method of silicon suitable for solar cells. To this end, commissioned by the Sunshine Projects Promotion Headquarters in MITI, a special work group was formed in the Japan Electrical Manufacturers Association in 1978, and it inaugurated a variety of research programs as part of Sunshine Project.

The Group investigated the manufacturing methods of semiconductor grade silicon (SEG-Si) and the development of solar grade silicon (SOG-Si) in foreign countries. They concluded that the most efficient method of developing such materials was the hydrogen reduction process of trichlorosilane (TCS), using a fluidized-bed reactor (FBR). The reasons were three: TCS had been proved in a number of studies to be an appropriate material for this purpose; the budget was insufficient to test several processes simultaneously; the hydrogen reduction process seemed to have high feasibility for practical application as revealed by studies conducted thus far.

This process was viewed as meeting the following conditions:

a. The process is suited to mass production, an essential point for future development.

b. The process reduces manufacturing costs to a greater extent than conventional SEG-Si manufacturing processes.

The low-cost manufacture of polysilicon requires cost reductions of raw materials, energy, labor, and capital.

Carefully reviewing these conditions, the work group reached the following conclusions:

a. Polysilicon manufacture should be based on the hydrogen reduction of TCS process. The chlorosilane hydrogen reduction process is the optimum method of obtaining higher-purity SOG-Si, has previously been studied as the SEG-Si manufacturing process, and has already been used in practical manufacture.

   Fig. 1 compares the thermodynamic characteristics of hydrogen reduction of silicon tetrachloride (STC), TCS and dichlorosilane (DCS). The results for silicon yields suggest that the use of TCS is more advantageous than STC and in turn the use of DCS is more advantageous than TCS. The conclusion was that TCS, which is already widely used, should be studied further in the project and that the use of DCS is not yet practical for industrial mass production.

b. STC, a by-product of the manufacture of polysilicon from TCS, should be recycled into TCS via hydrogenation. The process step of recycling STC to prepare TCS removes the limitation of having to locate the silicon manufacturing process near a plant for producing silicon compounds from the STC by-product.

c. The FBR process should be adopted. The Siemens process for manufacturing SEG-Si is considered to have the disadvantages of high thermal use and low production rate, which increase manufacturing costs. The FBR process is expected to improve these shortcomings.

The overall conclusion was that a development program should be based on the TCS-FBR process and the experimental program should be conducted in test facilities capable of producing 10 tons of silicon granules a year.

DEVELOPMENT OF LOW-COST SILICON MANUFACTURING TECHNOLOGY

In October 1980, the New Energy Development Organization (NEDO) was established to play a pivotal role in the promotion of new energy development. It was decided that one of its plans should focus on the development of a crystal silicon solar cell. The plan, requiring the development of low-cost silicon as a starting material for solar cells, adopted the conclusions proposed by the work group mentioned above.

NEDO divided the present process (the NEDO process) into two parts, commissioning the part for TCS manufacture to Osaka Titanium and the other for silicon granule manufacture to Shin-etsu Chemical. The respective assignments are shown in Fig. 2.

1. Development of Low-Cost TCS Manufacturing Technology

The two key points in this development project are as follows:

a. To produce TCS from hydrogen, metallurgical grade silicon (MG-Si) and STC (a bulk by-product of the hydrogen reduction of TCS) as expressed in the equation:

$$3SiCl_4 + Si + 2H_2 \longrightarrow 4SiHCl_3$$

b. To purify, at the lowest cost possible, the resulting TCS to a grade necessary and sufficient for use in solar cells.

1.1. Testing with small experimental apparatus

From 1980 to 1981 a number of tests were conducted to determine the conversion potential of STC to TCS using a small experimental fixed-bed reactor and a 10 cm-diameter FBR.

The fixed-bed reactor was used to measure the reaction temperature, the gas chemical composition, the residence time requirement and the catalyst effectiveness. The results were then checked using the fluidized-bed reactor which was also used to measure the effects of pressure.

1.2 Operation of TCS 200 T/Y experimental apparatus

Based on the test results obtained using the experimental reactors, further tests were undertaken beginning in October 1982, using the 200 tons/year test manufacturing apparatus shown in Tables 1 and 2, and Fig. 3. (1)

In this facility, TCS is evaporated in a steam-heated evaporator, mixed with hydrogen, heated to 650 to 700°C by a heater at the bottom of the reactor, and released into the fluidized-bed reactor filled with MG-Si seed particles. The fluidized-bed temperature is maintained at 500 to 600°C by the sensible heat of the gas.

The gas discharged from the reactor top is composed of 75 t9 77% STC, 23 to 25% TCS and 0.5% DCS. (3) The gas is then cooled to -35°C, condensed and recovered. The condensate is transferred to the distillation plant where the STC is removed in the first column, low-boiling point impurities in the second column, and high-boiling point impurities in the third column; the purified product is TCS.

The operational results, shown in Table 3, indicate that with all targets achieved, the present manufacturing process can produce TCS at the rate of 200 tons/year. (4)

An analysis of TCS obtained via this process produced the results listed in Tables 4 and 5. (7) Analytical samples were prepared by hydrogen-reducing TCS and float-zoning the resultant silicon rods. The samples thus obtained were then measured for electrical resistance to estimate the donor and acceptor concentrations. TCS was analyzed by atomic absorption measurements to determine its metallic impurities.

2. Development of TCS Hydrogen Reduction Technology

The goal of the project is to achieve a reduction of energy-use and improved productivity, both essential for low-cost silicon manufacture, by replacing the Siemens bell jar with a FBR.

2.1. Testing with small experimental apparatus

In 1981, an experimental apparatus of 0.5 ton/year capacity was developed to study the basic structure of the FBR. Tests conducted until the following year revealed the following results: (8), (9)

a. Quartz tubes used for FBRs ruptured during experimental runs due to silicon deposits on the tube interior. Therefore, SiC-Si tubes (prepared by sintering a SiC-Si mixture) with a thermal expansion coefficient nearly equal to that of silicon were substituted.

b. It was found that the silicon deposits could be removed by exposure to a $HCl-SiCl_4$ mixture at high temperature.

c. The problem of the clogging of the gas injection nozzle by silicon deposits was alleviated by developing and installing a water-cooled bottom plate.

d. The reactor power consumption was approximately 30 kwh/kg of Si; the diameter of the product granules was 0.8 to 1.5 mm; and the product quality was indicated by measurements of the conversion efficiency of solar cells prepared from 3" diameter Czochralski single crystals grown from the FBR granules; these values ranged from 10 to 12%.

e. A number of methods were tested for the preparation of silicon seed particles. These included crushing and the use of high frequency plasma for melting and spraying. Crushing using a roll-crusher was found to be the most appropriate method.

2.2. Operation of 10 tons/year experimental FBR apparatus

This apparatus has been undergoing improvement since its completion in August 1982, and continues to be used in test operations. Table 6 lists the major apparatus dimensions and reaction conditions. (6) Table 7 summarizes the operational results for fiscal 1984. (5)

Two of the conventional problems associated with the FBR were alleviated. Clogging of the bed was eliminated by the improvements of the fluidizing conditions and of the bottom plate shape, while silicon deposition on the walls was decreased by improving the reaction temperature control technique.

The most serious problem in the present project was the rupture of FBR tubes. Based upon the findings obtained from the tests with the small experimental apparatus, an attempt was made to use SiC-Si material. It was found, however, that the silicon in the SiC-Si reacted with the HCl gas, thus causing a deterioration of the tube (a problem known as "overcleaning"). As a consequence, the tube became permeable, allowing the diffusion of impurities through microscopic pores.

Accordingly, another attempt was made to use a tube that had been CVD-coated with SiC on the tube interior. Although this basically solved the problem, fragility due to a difference in the thermal expansion coefficients of the CVD layer and the SiC-Si substrate remained unavoidable. This problem is considered to be the most formidable obstacle to enlarging the apparatus.

With regard to seed production, two procedures were attempted based upon the experimental results: crushing high-purity silicon using a roll crusher and then screening the resulting material using a quartz sieve in clean nitrogen gas.

The process flow and the material-product balance are shown in Fig. 4. (8) The yield was approximately 70% and the roll wear was approximately 1 g per kg of crushed material.

The target quality of product silicon granules in the present project was P-30 or N-10 ohm-cm in specific resistance, and 10 μsec. in lifetime, as measured in the Cz crystal. However, the results showed specific resistance of between N-10 and 20 ohm-cm and a lifetime of between 10 and 30 μsec. Chemical composition analyses of the product granules are shown in Table 8. (5)

It was proved that the silicon granules obtained in this project could be used to achieve 12.7% conversion efficiency in polycrystalline solar cells, demonstrating that the granules have satisfactory quality as SOG-Si.

OTHER PROCESSES

NEDO has inaugurated two new development projects for SOG-Si manufacturing technology. One, called "TCS manufacturing technology by quenching", commissioned to Denki Kagaku Kogyo; this new method uses silica produced in Japan, whereas the NEDO process and other conventional processes use imported MG-Si to manufacture TCS. TCS is manufactured via the following two steps. This process is undergoing testing using a 4 kg/h apparatus.

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

$$SiCl_4 + H_2 \longrightarrow SiHCl_3 + HCl$$

The other project underway at Nippon Sheet Glass aims to produce low-cost SOG-Si using low-grade silica sand, found in abundance in Japan. In this method, silica sand is purified into high-grade silica, which is then carbon-reduced in an arc furnace to produce SOG-Si. Since silica is purified in the form of water glass, the process is called the "water glass method".

As shown in the Fig. 5 flowchart, the starting material is silica sand, a material used in sheet glass, containing 96 to 97% SiO_2. (10) The sand is physically purified into nearly 99.9% purity silica, mixed with an alkali oxide source, such as sodium carbonate, melted in an autoclave and turned into water glass. Water glass thus obtained is subjected to acid treatment to form silica deposits. The resulting silica, washed with acid and water, is of high purity. Table 9 indicates changes in impurity levels of the silica sand before and after physical purification. (6) Table 10 compares the analytical results of silica purity in physically purified silica and water glass silica currently on the market. (10)

Purification testing is being conducted using a 10 kg SiO_2/day apparatus. Testing is also underway to characterize the carbon-reduction of silica using a small arc furnace (55 KVA), an improved version of the conventional arc reduction.

FUTURE STRATEGIES

Fig. 6 shows the changes in the price of marketed solar cell modules and the future target of the Sunshine Project. The figure indicates that after the module cost is reduced to 500 yen/wp ($2.30/wp), these modules will begin to sell as dispersed-type PV generation system (primarily in place of diesel generators). This will be the first step toward the wide use of the solar power system as a general-purpose power supply. Subsequently, it is anticipated that further cost-cuts will result from the mass production effect. As a consequence, many efforts are underway to establish low-cost technologies for polysilicon production and high efficiency solar cell fabrication with the goal of a solar cell module price below 500 yen/wp ($2.30/wp) by the early 1990's.

Currently a plan is being reviewed to construct and conduct test operation of a pilot plant based on the TCS-hydrogen reduction FBR technology to produce silicon granules. This would be done with the support of NEDO and the Sunshine Project Promotion Headquarters.

In this plan the pilot plant would be of a 80 to 100 tons/year silicon granule production capacity, its construction would begin in 1987, and the operation results would be reported in 1990. A successful demonstration would be a major step toward the commercialization of this process.

The FBR tubes to be used in this development will be of 40 to 60 cm diameter and the production capacity per reactor will be 40 to 50 tons/year.

The cost target in manufacturing silicon granules in this plant is set at 6000 to 8000 yen/kg ($27.90 to $37.20). To achieve this target, the following technical goals will have to be realized.

a. Development of a large-diameter FBR capable of sustaining long-term, continuous operation.

b. Demonstration of the fully-closed system connecting the TCS production and hydrogen reduction processes. (Research on each process step is under way independently.)

c. Establishment of the optimum operational conditions and the automatic control technology for a large scale plant.

Especially important among these is the development of large-diameter, high-reliability FBR tubes. This will be a key step in scaling up the present process. For this purpose, it is essential to select the most appropriate material for the tubes. The estimate of the polysilicon manufacturing cost for a 1000 MT/year plant based on this process is 4300 yen/kg ($20./kg).

In the water glass method, expected as the next-generation SOG-Si manufacturing method following the TCS-hydrogen reduction method, the cost target is set at 2000 to 3000 yen/kg ($9.30 to $14.00). By 1986 the development project will have finished evaluating the results thus far and will have decided upon future strategies.

The mass utilization of solar cells is about to occur. It is anticipated that the projects mentioned above will serve to establish the low-cost silicon manufacturing process, thus contributing to the cost reduction of solar cells.

ACKNOWLEDGEMENTS

Before concluding this report, we would like to thank the Sunshine Project Promotion Headquarters, NEDO, Shin-etsu Chemical and Nippon Sheet Glass for giving us advice and the relevant data.

We also want to express our gratitude not only to JPL but also to other organizations all over the world for their discussions of the developments of low-cost polysilicon processes.

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Table 1. Experimental TCS Manufacturing Equipment

Hydrogenation reactor		
Reactor type		Fluidized-bed
Inner diameter	(cm)	25
Reactor Height	(cm)	500
Running conditions		
Bed depth	(cm)	300
Feed gas molar ratio	($H_2/SiCl_4$)	1.5 to 3.0
Hydrogenation temp.	(^oC)	550
Hydrogenation pressure	(kg/cm^2G)	7.5 to 8.0
Catalyzer		CuCl

Table 2. Experimental TCS Purification Equipment

First distillation column		
Column inner diameter	(cm)	40
Column height	(cm)	910
Distillation stage		25
Second distillation column		
Column inner diameter	(cm)	40
Column height	(cm)	1,640
Distillation stage		50
Third distillation column		
Column inner diameter	(cm)	40
Column height	(cm)	1,640
Distillation stage		50

Table 3. TCS Manufacturing Operation Results

Item		Targets	Results
Conversion			
Conversion ratio	(mol%)	28.0	28.6 max
Production rate	(kg/Hr)	28.5	31.7
Power consumption	(kwh/kg.TCS)	2.7	*2.7
H_2 consumption	(Nm^3/kg.TCS)	0.11	0.094
MG-Si consumption	(kg/kg.TCS)	0.06	0.058
Distillation			
Steam consumption	(kg/kg.TCS)	8.0	5.6
Production rate	(kg/Hr)	28.5	31.7

* includes distillation

Table 4. TCS Quality

	One-pass FZ in Ar			Eight-pass FZ in Vac		
Lot	Specific resistivity (ohm-cm)	|Nd-Na| (ppba)	Lifetime (μ-sec)	Specific resistivity (ohm-cm)	Boron (ppba)	Donor Concentration Nd (ppba)
1	N- 151	0.64	80	P-1100	0.26	0.90
2	N- 255	0.38	100	P-3170	0.09	0.47
3	N- 258	0.37	130	P- 620	0.46	0.83
4	N- 172	0.56	80	P-1190	0.24	0.80
5	N- 150	0.64	70	P-3560	0.08	0.72
6	N- 250	0.38	25	P- 470	0.61	0.99
7	N- 150	0.64	50	P- 890	0.32	0.96
8	N- 327	0.29	60	P- 520	0.55	0.84

Table 5. Metal Impurities in TCS

(ppba)

Lot	Ti	Al	Fe	Ni	Cr	Cu	V
1	<20	<0.4	50	<0.2	0.3	<1	<5
2	<20	<0.4	130	0.7	0.3	<1	<5
3	<20	2	28	<0.2	0.5	<1	<5
4	<20	<0.4	210	<0.2	1.0	<1	<5
5	<20	<0.4	53	<0.2	0.9	<1	<5
6	<20	<0.4	15	<0.2	1.5	<1	<5
7	<20	0.5	11	1.1	3.7	<1	<5
8	<20	1.3	12	<0.2	0.7	<1	<5

Table 6. Basic Specifications with Capacity of 10 Tons/Year

Items		Planned Specification
Reactor type		Fluidized bed
Reactor inner diameter	(m)	0.21
Reactor height	(m)	2.5
Fluidized bed height	(m)	1.1 to 1.2
Feed gas, $SiHCl_3/H_2$		40/60
Reaction temp.	(^{o}C)	1,000 to 1,100
Heating system		External, SiC heater
Si yield	(%)	about 20
Power consumption	(kwh/kg.Si)	30
Si seed diameter	(mm)	0.25 to 0.5
Grown silicon diameter	(mm)	0.8 to 1.5
Off-gas	(CS and H_2)	Recovered and recycled

Table 7. Silicon Granule Manufacturing Results
(1984)

Items		Targets	Results Overall*	Best**
Total Reaction time	(Hr)	-	4,377	632
Manufactured Si	(kg)	-	8,349	1,504.7
TCS concentration	(%)	-	36.5	42.3
Power consumption	(kwh/kg.Si)	30	28.32	21.30
TCS consumption	(kg/kg.Si)	20	18.72	18.94
Si yield	(%)	20	18.3	21.5

* yearly performance

** best performance

Table 8. Analysis of Si Granule

(ppb)

Lot	Sample	Fe	Cu	Al	Cr	Mn	Mg
A	17	288.8	23.8	90.9	74.4	2.1	50.3
B	11	204.1	37.7	41.4	5.5	nd	20.5
C	27	241.9	76.9	nd	51.7	0.9	38.9
D	17	182.1	45.9	nd	16.5	nd	36.1
E	29	244.5	15.9	nd	2.9	nd	51.5

nd: not detected.

Table 9.

Analysis of Silica Sand for Sheet Glass and Physical Purification Product

	Impurities (ppm W)								SiO_2
	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	ZrO_2	Na_2O	K_2O	(%)
silica sand for sheet glass	19,000	1,500	642	277	364	20	947	10,480	96.7
physical purification product	270	40	70	30	9	3	20	20	99.9

Table 10. Impurity Level of Starting Material and Purified Silica

(ppm)

Impurities	Starting material		Purified silica	
	A	B	A	B
B	--	--	<1	<1
Na	--	--	0.9	1.0
Al	5,200	457	<3.5	<3.8
P	--	--	<1	<1
Ca	27	38	0.8	0.5
Ti	98	36	0.9	0.6
Fe	330	68	<0.5	<0.5
Zr	31	<7	<0.6	<0.6

A: water glass (whose impurity level was calculated in terms of silica.)

B: upgraded silica after physical purification

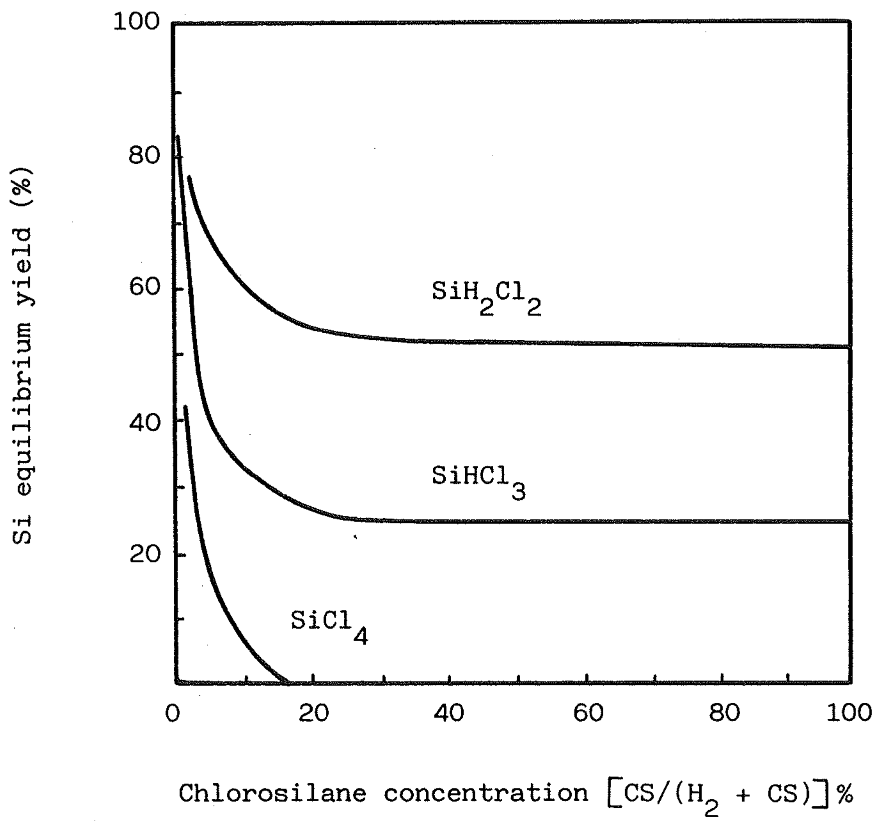

Fig. 1. Chlorosilane Concentration and Si Equilibrium Yield

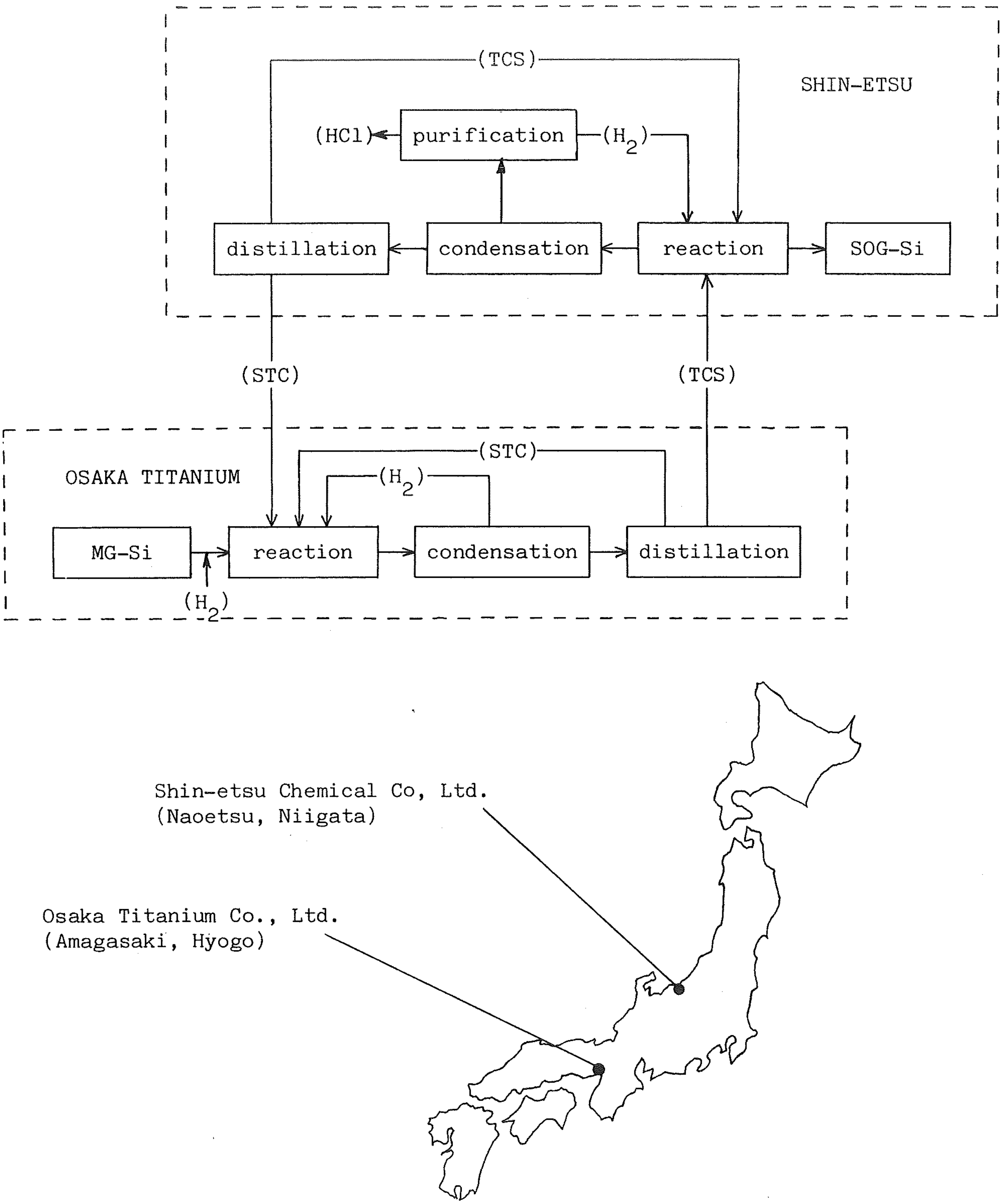

Fig. 2. Allotted Task of Low-Cost Si Manufacturing Technique Development

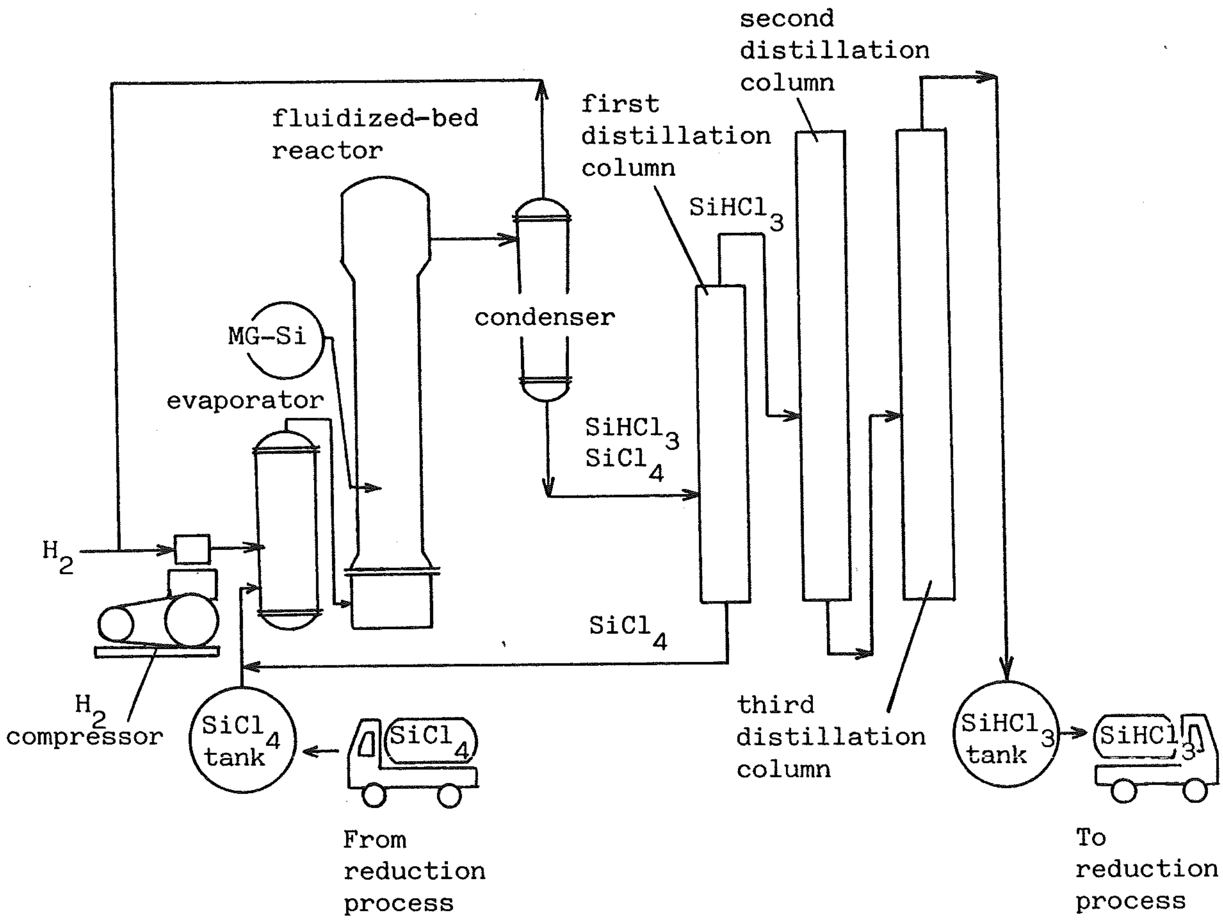

Fig. 3. Experimental TCS Manufacturing Equipment

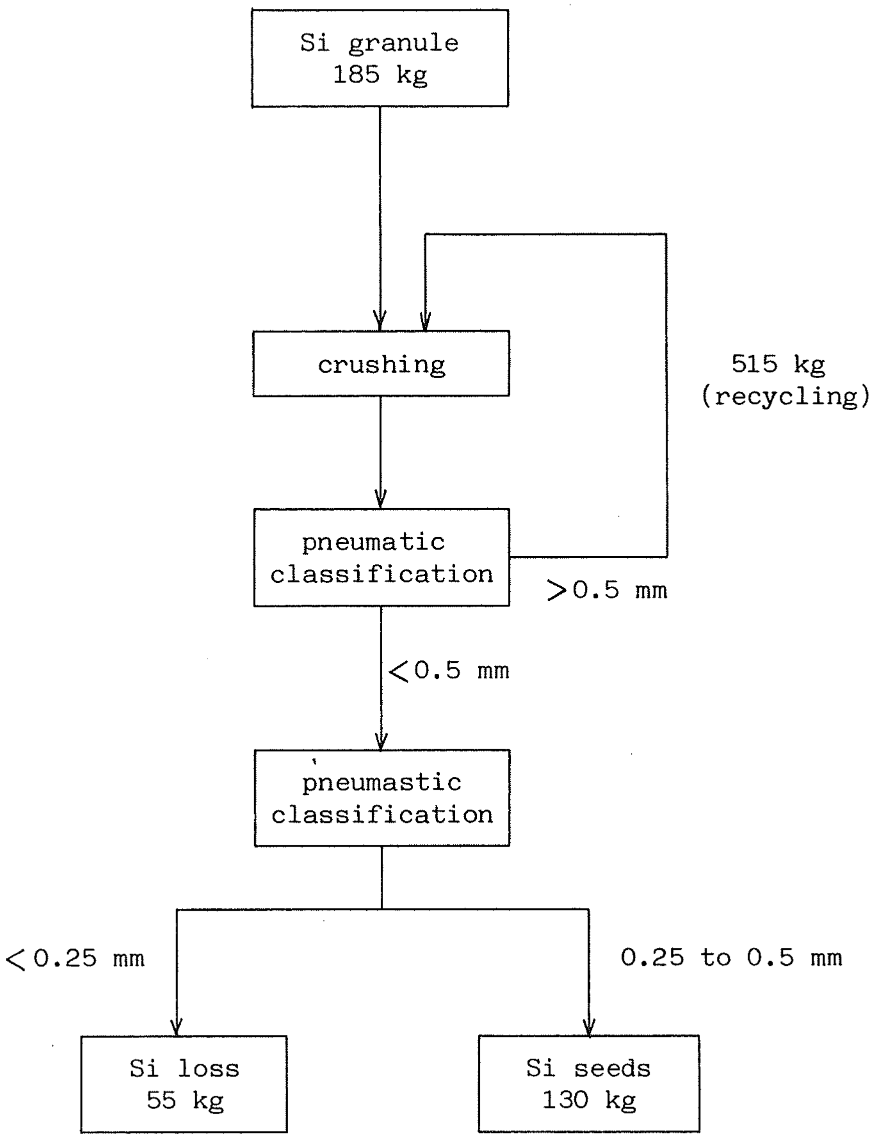

Fig. 4. Material Balance in Seed Preparation

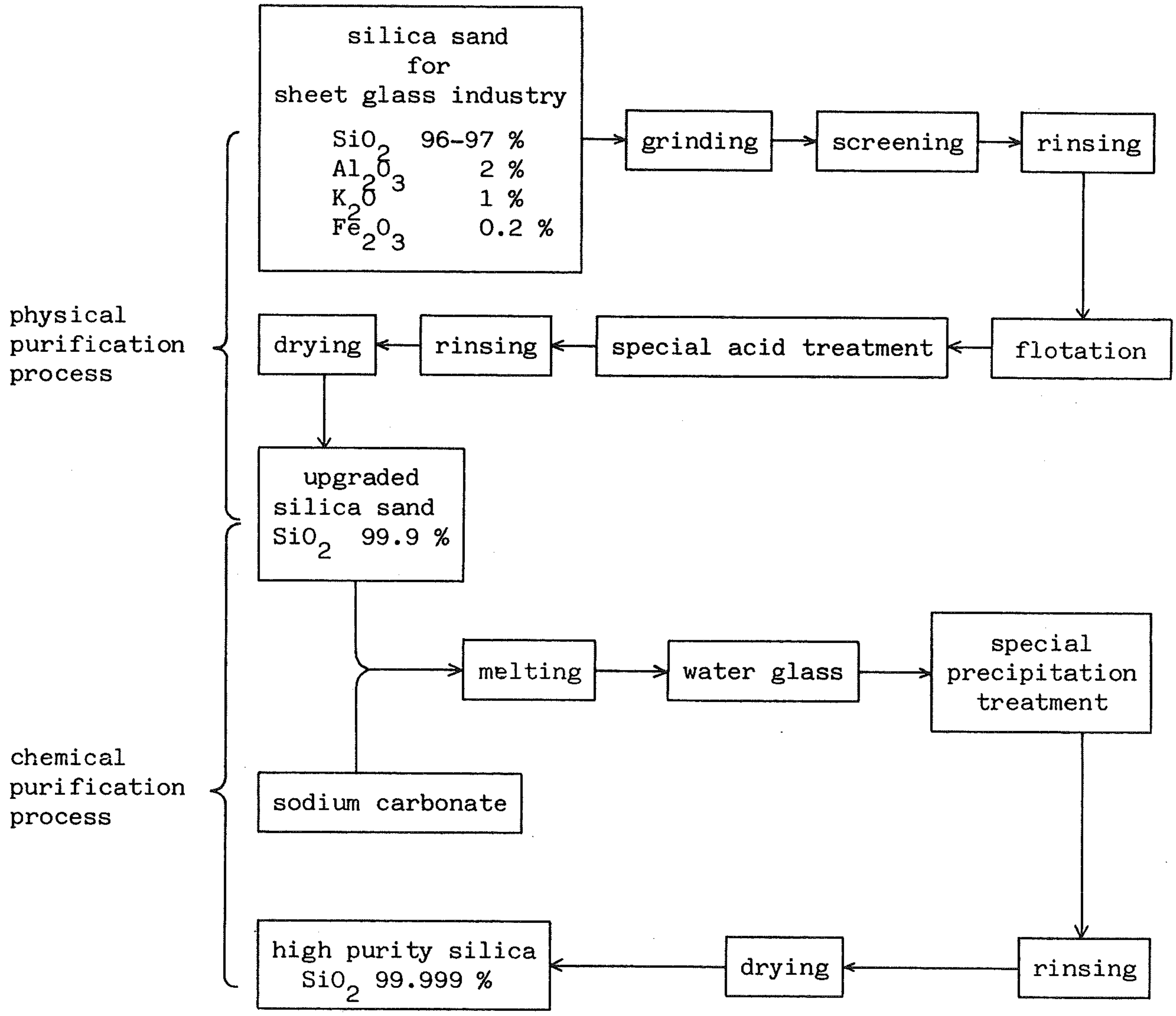

Fig. 5. Water Glass Method

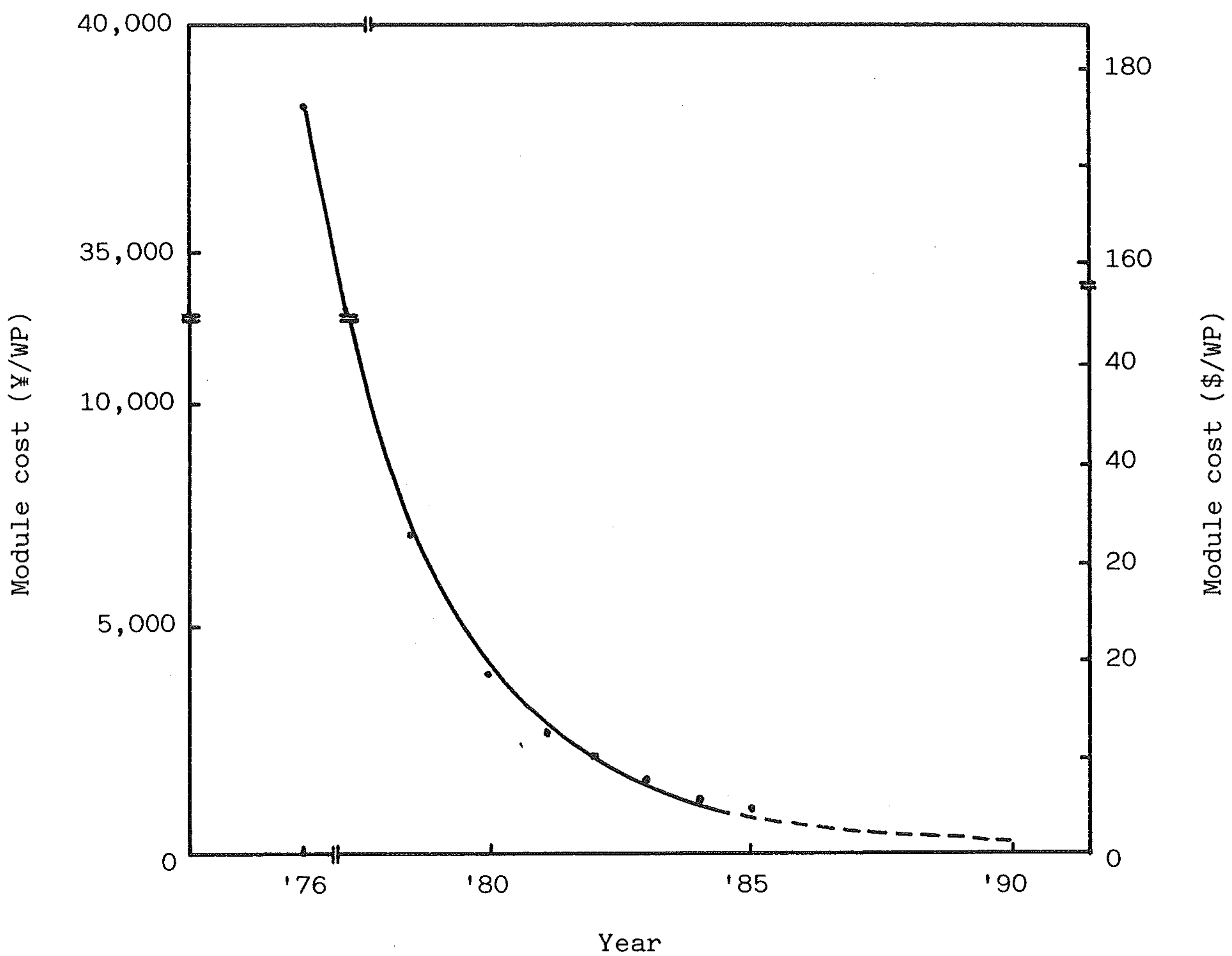

Fig. 6. Cost of Solar Cell Modules

(exchange rate : ¥215/$)

omit

DISCUSSION

HSU: What is the purity of your solar-grade silicon?

NODA: That is described in detail in the paper, so please refer to the paper.

LEIPOLD: Do you know what limits the purity of the fluidized-bed reactor product? Is it the trichlorosilane gas, the seed, or the reactor?

NODA: The product purity is determined by the composition and quality of the reactor tube.

LORD: How much carbon is there in the material?

NODA: Which material do you mean? Do you refer to the granules? We are achieving NEDO's target. Therefore, in that respect, we have not encountered any major problems in the quality of granules.

LORD: Approximately how much carbon is there in the crystals after you pull them?

NODA: We had a slight problem in carbon concentration, but the problem has been solved. The target for cell efficiency was initially set for 12%. When we try to drive up to 14%, we may encounter some problems, but at least the present efficiency target has been met.

LORD: Do you think it's possible to use this process to produce electronic-grade silicon?

NODA: My understanding is that everyone here has a strong interest to see our process applied to produce electronic-grade material. We would like to see that happen too.

AULICH: Did I understand you correctly that you are planning to produce 100 tons of these granules in 1990? And if the production is satisfactory, you will then decide on a 1000-ton plant? Is that correct?

NODA: The initial target was for 1000 tons. However, the Japanese government is also encountering deficits, so the project has been scaled down to 500 MT, and it may come down further to a smaller size. However, a 100 MT plant has been committed for 1990.