DEVELOPMENT OF THE SILANE PROCESS
FOR THE PRODUCTION OF LOW-COST POLYSILICON

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INTRODUCTION

Union Carbide Corporation (UCC) has been a major participant in the Jet Propulsion Laboratory (JPL)/Department of Energy (DOE) Flat-Plate Solar Array (FSA) Project to develop the technology for producing low-cost polysilicon for terrestrial photovoltaic solar cell applications. Based on its technology developed over many years of research activities, UCC responded to a request for proposal from JPL to conduct process feasibility studies aimed at producing polycrystalline silicon in accordance with stringent economic goals of the Solar Array Project, and was awarded a contract in late 1975. This contractual work progressed through several phases, culminating with the final design of a 100 metric tons per year Experimental Process System Development Unit (EPSDU). This pilot plant was originally to be installed on the site of a UCC facility in East Chicago, Indiana. However, shortly after the start of its construction, the activity was stopped because of contract-funding reductions. By mutual agreement between UCC and DOE, it was decided to relocate EPSDU to Washougal, Washington, and continue the pilot plant program using UCC funds as a first step in the commercialization of the silane to silicon process. A licensing agreement was arranged with Komatsu Electronic Metals of Japan to obtain commercially proven technology for decomposing silane to produce polycrystalline silicon.

Construction of the silane to silicon EPSDU was completed in 1982, and it was operated successfully to produce silane and polysilicon of exceptionally high purity for the electronics industry. Based on the original design data base developed under the JPL/DOE program, UCC constructed a 1200 metric tons per year capacity commercial plant in Moses Lake, Washington. This plant was brought on stream in early 1985, and is currently supplying high purity polysilicon to the industry.

Early in the JPL/DOE program, it was recognized that the traditional "hot rod" type deposition process for decomposing silane is energy intensive, and a different approach for converting silane to silicon was required to address the low-cost goals. A fluidized bed process was chosen to be the most promising method for this purpose, and its development was pursued with a laboratory process development unit (PDU). Several encouraging test runs have been conducted to date on the fluid

bed PDU and this technology continues to be a very promising one for producing low-cost polysilicon.

This paper will discuss the UCC silane process and the research and development (R&D) work on fluidized bed silane decomposition conducted under JPL/DOE sponsorship.

SILANE PROCESS

The UCC silane process is based on many technical innovations in proven chlorosilane chemistry to achieve very high purity levels in the product. The use of silane as a single reactant instead of a binary trichlorosilane-hydrogen mixture as in the traditional Siemens Process has the following significant advantages:

- The boiling point of silane is lower than that of all the chlorosilanes and impurities such as the chlorides and hydrides of boron, phosphorus, and arsenic. Consequently, it is easier to purify silane and it can be purified to higher levels than any of the chlorosilanes.

- Silane can be totally decomposed to produce high-purity silicon and hydrogen in a single pass. since silane is converted to silicon in single-pass operation, the possibility of contamination is minimized.

- The byproduct hydrogen can be readily separated from the solid silicon product, and is electrically inactive.

- The absence of corrosive chlorine compounds in the product stream minimizes the chances of contamination, and simplifies material selection.

The silane to silicon process starts with metallugical grade (m.g.) silicon and refines it to semiconductor grade product in a series of reaction and purification steps. The process consists of three major steps:

- Hydrogenation, where silicon, silicon tetrachloride (STC), and hydrogen react at high temperature and pressure to form trichlorosilane (TCS),

- Redistribution, where the hydrogen and chlorine atoms are redistributed within the chlorosilane molecules, eventually yielding high-purity silane, and

- Decomposition, where purified silane is thermally decomposed to yield semiconductor grade polycrystalline silicon.

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The process is described by the flow diagram shown in Figure 1. M. G. silicon, STC and hydrogen are reacted at high pressure and temperature in the hydrogenation reactor to yield TCS:

$$Si + 2H_2 + 3 SiCl_4 = 4HSiCl_3$$

This reaction is carried out in a fluidized bed consisting of fine silicon particles. The hot product gases leaving the reactor are quenched to their dew point in a venturi contactor. The quenched two-phase mixture enters a waste settler tank where many of the metal contaminants form insoluable complexes with one another and settle to the bottom. Vapors from the settler are cooled in a quench condenser which condenses the chlorosilanes. The condensed 'crude' TCS is sent to a storage tank, and the uncondensed hydrogen is recycled to the hydrogenation reactor. The heavy non- volatile impurities and elutriated silicon fines are periodically purged out of the settler to the waste treatment area.

The next major processing area is distillation/redistribution. In this section, TCS is redistributed eventually forming silane, and the impurities are rejected from the process streams. The redistribution reactions take place in two packed-bed liquid phase reactors containing an ion-exchange resin which serves as a catalyst for the reactions. In the TCS redistribution reactor, dichlorosilane (DCS) and STC are produced according to the reaction,

$$2SiHCl_3 = SiH_2Cl_2 + SiCl_4.$$

In the DCS redistribution reactor, DCS is redistributed to form monochlorosilane (MCS) which rapidly redistributes to form silane,

$$2SiH_2Cl_2 = SiHCl_3 + SiH_3Cl$$

$$2SiH_3Cl = SiH_4 + SiH_2Cl_2.$$
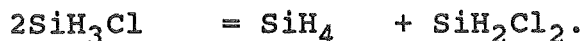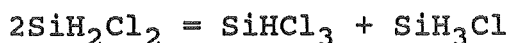
The remainder of the purification train consists of four distillation columns which provide the required feed composition for the reactors and reject the impurities.

The first distillation column is a light-gas stripper. It receives the crude TCS product from the hydrogenation reactor and removes dissolved gases such as residual hydrogen from hydrogenation and inert gases from process purges.

The TCS column separates TCS and DCS from STC. It receives the stripped crude TCS from the stripper and the product from the TCS redistribution reactor. The distilled TCS-DCS mixture is fed to the DCS distillation column, and the STC bottoms product is recycled to hydrogenation.

The DCS column provides proper feeds to the redistribution reactors. It receives the TCS-DCS mixture from the overhead of the TCS column and the bottoms stream from the silane column. The bottoms product from the DCS column (primarily TCS) is fed to the TCS redistribution reactor, and the distillate, which is DCS with some MCS, is fed to the DCS redistribution reactor.

The silane column is designed to produce very high-purity silane while rejecting all chlorosilanes and any other contaminants. The feed stream to this column is the product from the DCS redistribution reactor. Silane is removed as the overhead product and is sent to storage tanks, while the bottoms stream containing the remaining chlorosilanes is returned to the DCS column. The silane column is keyed for separating silane from diborane which is the most volatile electronic contaminant in the system.

Silane thus produced is decomposed utilizing the technology acquired from Komatsu Electronic Metals of Japan,

$$SiH_4 \rightarrow Si + 2H_2.$$
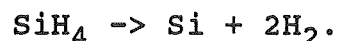
Heterogeneous decomposition of silane is accomplished on electrically heated seed rods which grow from an inital diameter of 7.5 mm to final diameters in the range of 80 to 100 mm. The byproduct hydrogen is recycled to hydrogenation.

POLYSILICON PURITY EVALUATION

Purity evaluation of polycrystalline silicon is accomplished by taking core samples from the polysilicon rod product, and zone-refining into small single crystal rods. Wafers sliced from the seed and tang ends of the single crystal rod are analyzed by Fourier transform photoluminescence (FTPL) spectroscopy at liquid helium temperature to obtain donor/ acceptor impurity concentrations in the material. Carbon and oxygen impurity levels are measured by Fourier transform infrared (FTIR) spectroscopy at liquid helium temperature. Resistivity values are obtained with a high-impedance four-point probe. Resistivity profiling of the sample single crystal ingot is done by a high impedance two point probe. The sample ingot is also analyzed for minority carrier lifetime.

Typical purity evaluation data for the present production grade silicon material are as shown below:

Boron	<0.06 ppba
Phosphorus	<0.30 ppba
Aluminum	Not Detected

Arsenic	Not Detected
Antimony	Not Detected
Carbon	<0.5 ppma
Lifetime	5 milliseconds
Resistivity	>1,000 ohm-cm

The above material is ideally suited for single crystallization by Czochralski or Float Zone method for semiconductor applications.

FLUID BED SILANE DECOMPOSITION

Fluid bed pyrolysis of silane involves heterogeneous decomposition of silane gas on hot silicon seeds to produce free-flowing particles of silicon. The method offers the potential for converting high-purity silane into pure silicon product at a cost which is consistent with the overall goals of the FSA program. Furthermore, since the fluid bed product consists of free-flowing particles, it can be directly processed in a Czochralski furnace where continuous growth by melt replenishment may be feasible.

Under the JPL/DOE program, UCC has been engaged in R&D work on deposition of silicon in a fluidized bed reactor. The goals of this program are to demonstrate the process feasibility, detemine a suitable operating window for the fluid bed reactor, conduct long-duration tests, and demonstrate silicon purity.

Several experimental runs have been conducted to date using a 6 inch diameter quartz-lined reactor and product samples have been produced for purity evaluation. A schematic of the fluid bed PDU is shown in Figure 2. The reactor assembly consists of a stainless steel shell with an internal high-purity liner. The reactor contains a bed of silicon seed particles which grow in size due to heterogeneous decomposition of silane. The reactor wall is heated with multi-zone resistance heaters which maintain the bed in the temperature range 600 to 700°C. The product is cooled and collected in bags.

Silane and hydrogen are pre-mixed in desired concentrations, and the mixture is fed to the reactor through a water-cooled gas distributor assembly. The gas velocity at the bottom of the fluid bed is approximately 3.5 times the minimum fluidization velocity. The effluent hydrogen in the PDU is cooled and vented after taking a small sample stream to a gas chromatograph which monitors the silane conversion in the fluid bed.

A number of long-duration test runs have been conducted, the longest single continuous run to date being of 66 hours duration. In these runs, the feed silane concentration was typically in the range of 25 to 30% in hydrogen, although concentrations up to 50% have been tested for short durations. The average silicon deposition rate was in the range 1 to 2 kg per hour. Seed particles of initial mean size 300 microns were grown to approximately 600 microns. The growth of larger particles, up to 1000 microns, is considered feasible.

Samples of seed and product particles were studied by scanning electron microscope and optical micrographs. The starting seed particles have an irregular shape with sharp edges. The product particles display a smooth rounded exterior surface with a ring-like, layered structure. The product particles have a dense and uniform deposition morphology with a bulk density of approximately 1.6 gm/cc.

The seed and product samples were analyzed for heavy metals by spark source mass spectrometry. The results are shown below for a typical test run H-02:

ELEMENT	SEED, PPMA	PRODUCT, PPMA
Fe	3	1
Al	10	2
Cr	0.05	0.03
Mn	0.3	0.1
Ni	< 0.5	< 0.5
Cu	$\leq$ 0.02	$\leq$ 0.02

It is clear that the product has less metallic contamination than the seed, indicating that the deposited growth layer is of higher purity. These data also support the use of a liner as an impurity barrier from the reactor walls since earlier results without a liner had shown metallic contaminant levels of over 100 ppm in the product samples.

Samples of seed and product from the fluid bed reactor (run H-02) were melted in a Czochralski furnace in an attempt to single crystallize them in two successive runs. The seed material yielded a polycrystalline ingot while the product sample resulted in a 3" diameter 21" long dislocation-free crystal, followd by 7" of dislocated single crystal and 4" of polycrystalline ingot. Wafers sliced from the top and bottom ends of the single crystal from the product sample were analyzed for donor/acceptor concentrations by Fourier Tranform Infrared Spectroscopy (FTIR) at liquid helium temperature. The wafers were also analyzed for electrical resistivity. The results are shown below:

	TOP END	BOTTOM END
Phosphorus, ppba	4.2	8.5
Boron, ppba	8.5	10.0
Arsenic, ppba	0.1	0.28
Aluminium, ppba	1.2	4.6
Antimony, ppba	< 0.02	0.07
Carbon, ppma	4.99	22.0
Oxygen, ppma	14.0	18.0
Calculated Resistivity, ohm-cm	50 P type	40 P type
Measured Resistivity, ohm-cm (average of 10 points)	87 P type	87.6 P type

It is clear that the donor and acceptor concentrations are in the parts per billion range. The results so far have indicated that the starting seed material is not of high purity, and is a major source of contamination. R&D work currently in progress aims at minimizing this contamination by preparing high purity seed material. Additional test runs using improved seed material will be conducted to establish fluid bed product purity.

CONCLUSIONS

The UCC silane to silicon process has produced both silane and polysilicon of exceptionally high purity. The silane technology developed under the JPL/DOE sponsorship has been successfully commercialized.

The fluid bed process for silane decomposition shows an excellent promise for producing high purity silicon material, consistent with the cost goals of the FSA project.

ACKNOWLEDGEMENTS

HYDROGEN RECYLCE

HYDROGEN RECYCLE

M.G. SILICON FEED

QUENCH CONDENSER

COOLING

120°C

-25°C SILANE

70°C

LIGHT GAS WASTE

HYDROGENATION REACTOR

500 C
515 psia

METAL CHLORIDE WASTE

STRIPPER COLUMN

96 psia

TCS COLUMN

55 psia

DCS COLUMN

320 psia

50°C
550 psia

SILANE COLUMN

360 psia

SILANE DECOMPOSITION REACTOR

70°C
85 psia

100°C

HEAT

HEAT

STC RECYCLE

TCS REDISTRIBUTION REACTOR

DCS REDISTRIBUTION REACTOR

SILICON PRODUCT

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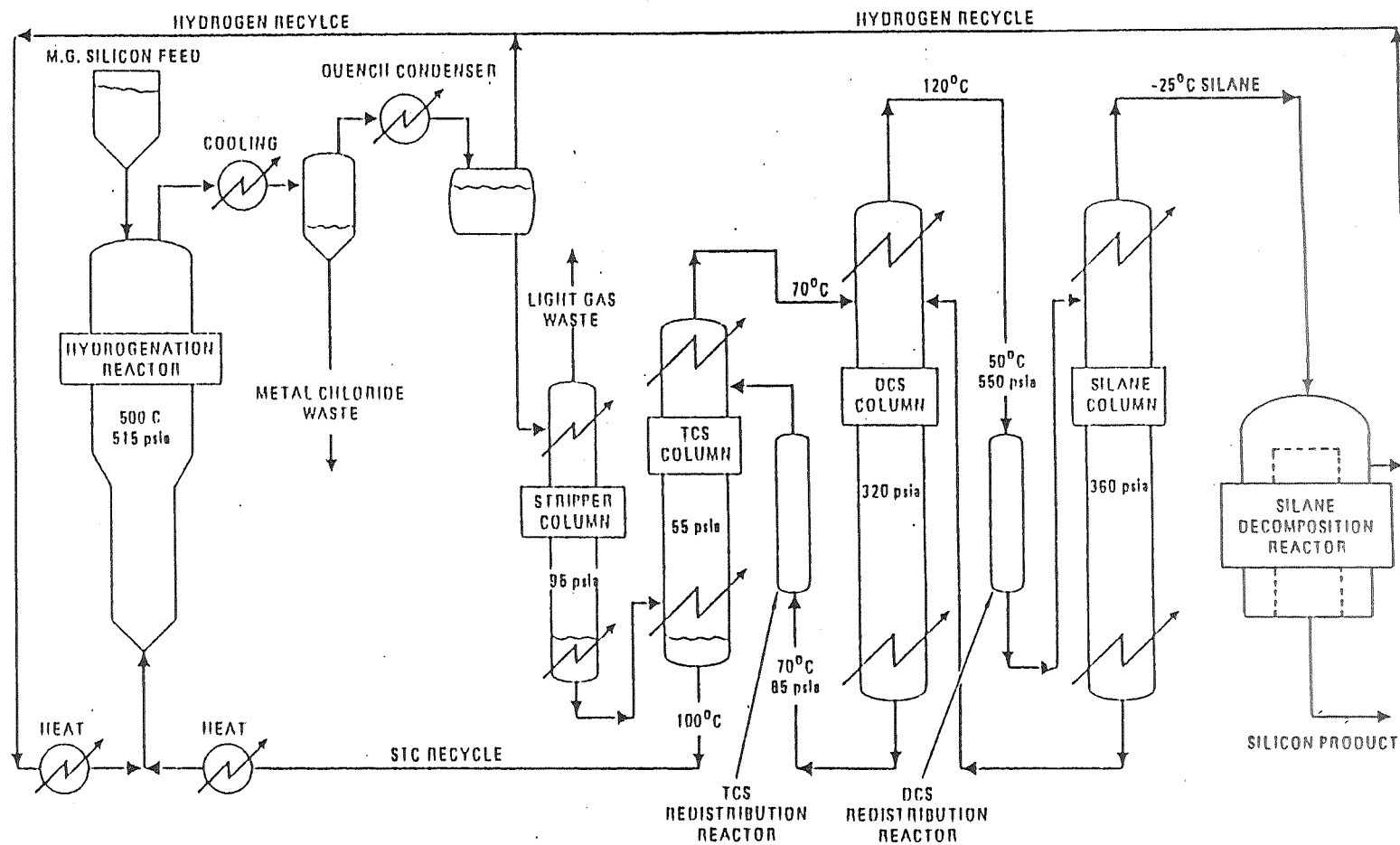
FIGURE 1: Flow Schematic of Silane to Silicon Process

CWR

EFFLUENT COOLER

CWS

EFFLUENT

EXPANDED HEAD

FILTER HOPPERS

REACTOR

SILANE SUPPLY

GAS DISTRIBUTOR

CWR

BOOT SECTION

CWS

POWDER

HYDROGEN SUPPLY

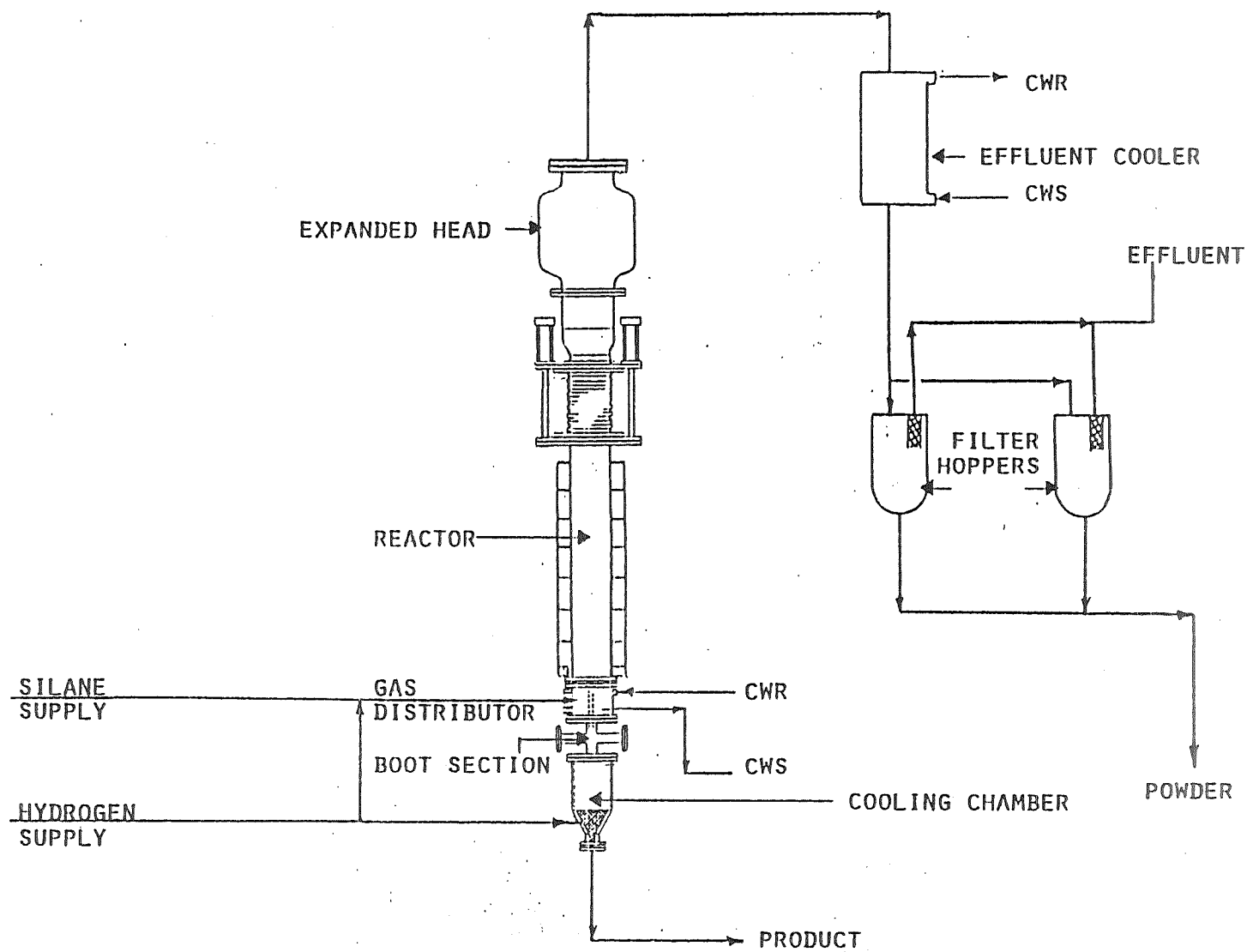COOLING CHAMBER

PRODUCT

FIGURE 2: FLUID BED PROCESS DEVELOPMENT UNIT

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SANJURJO: Professor Carl Yaws has just addressed the problem of homogeneous nucleation in the Komatsu reactor. Would you describe the nucleation problem further? What is its impact on production?

IYA: Well, I'm not prepared to discuss the Komatsu reactor, per se. Professor Yaws referred to a paper which was published in the Journal of the Electrochemical Society that describes the conditions under which silane can be decomposed either homogeneously or heterogeneously, and I refer you to that paper.

SCHWUTTKE: Do I understand correctly that Union Carbide plans to have a 1998 production capacity of 5500 MT/year? If I'm correct, this corresponds approximately to the total world capacity today. Is this correct?

MAYCOCK: Dr. Pellin is going to discuss this in depth later. The answer is essentially yes.

SCHWUTTKE: I'm somewhat confused by your presentation of the data for the purity of the silicon produced in the Union Carbide silane process. Would you describe more carefully the silicon products from the Komsatsu reactors and the fluidized-bed reactor?

IYA: The data I gave for the silicon from the EPSDU and from the Moses Lake commercial plant showed that these products are very high-purity, semiconductor-grade materials. Union Carbide is marketing the commercial product throughout the world. On the other hand, the data for the silicon granules from the experimental fluidized-bed reactor show that the purity is not semiconductor grade. In our experimental program, we also intend to work toward meeting the semiconductor-grade purity levels for the fluidized-bed product.

AULICH: You mention that your process yields electronic-grade silicon. We already have an electronic-grade silicon produced by the Siemens process which is too expensive. Do you have any plans of offering so-called solar-grade silicon at a considerably lower price, or are you only looking at the electronic market?

IYA: This is a question that should be answered by our marketing people. I'm certainly not in a position to do that.

KOINUMA: What are the main reasons preventing you from extending the duration of the fluidized-bed reactor operation and also growing particles larger than 800 μm?

IYA: We have been conducting essentially research and development work using a laboratory unit, and there are time limitations for conducting these experiments. But, aside from that fact, I think we will probably run into some inherent limitation on the particle size as we grow larger particles. Some of the experts in fluidization point out that

fluidization will become difficult. We don't know what the limit is. So far, the particles have been grown to about 800 μm size.

KOINUMA: Could you also tell me how you collected the fine particles? I think you mentioned that about 5.5 to 6% of the product is fine particles. How do you collect these fine particles?

IYA: We have filters located downstream of the process, and at the end of the run we collect the particles. We then weigh the mass to determine the fines content.

FUJII: What improvement do you seek in the preparation of seed particles?

IYA: We are trying to implement a cleaning method that involves acid cleaning and handling the seed material so that it remains in a fairly pure state.

MAYCOCK: I think that we should notice the location of their plant. Our Japanese paper showed electricity cost 15 yen/kWh which is approximately 6¢. Dr. Yaws used 5¢ in his economic analysis, and I would guess that the Union Carbide, Washougal plant, is about 2¢. Is that correct? It used to be 9 mils. Before the energy crisis, it was 9 mils, and then it went up to almost 30 mils during the shortage of water. Now, with water running over the dams and power to burn, I think they are probably back to something around 20 mils cost. Those of you doing economics on Union Carbide need to find out what that cost is.