LARGE AREA SILICON SHEET TASK LOW-COST
SILICON SOLAR ARRAY PROJECT

Sixth Quarterly Progress Report
April 4, 1977—July 1, 1977

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MASTER

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by

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11 July 1977

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ABSTRACT

- Silicon ribbons were grown in the presence of some air back-streaming and were consistently polycrystalline with little evidence of oriented growth from the seed.

The problem of back-diffusion of air from the exit port has been eliminated, and clean growth conditions, as determined by silicon wafer film test, have been obtained in the redesigned seeded growth furnace. This furnace developed a water leak in the cooling nozzle, so it has not as yet been used to grow silicon.

A new, vertical seeded growth furnace, which permits the seeding and initial crystal growth to take place below the alloy surface, has been designed and is being built.

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Section 1

INTRODUCTION

This research program began January 6, 1976. Its objective is to demonstrate the feasibility of the floating substrate sheet growth process for the growth of silicon sheet. This process is an approach to the formation of single-crystal silicon by direct epitaxial conversion from a gaseous silane. Incoming feedstock gas impinges upon a silicon substrate, which is floating upon a thin pool of liquid tin. Single-crystal silicon grows to the desired thickness by means of vapor phase epitaxy. Nucleation of fresh substrate silicon takes place by rapid growth from the edge of the growing sheet into a region at the surface of the liquid tin, which is supersaturated with silicon. The process lends itself to continuous operation, with the growing sheet being continuously withdrawn from the growth zone.

Since the epitaxial growth of silicon has already been extensively studied, we have focused our effort upon studies of the nucleation and growth of substrate silicon from the supercooled Sn-Si melt. Our investigations included studies of (1) supercooling, (2) crystal growth from the supercooled Sn-Si alloy, (3) silicon uptake into tin from silanes, and (4) surface growth. The goals of this contract are the growth via this process of single-crystal silicon having 0.5 cm² area and the determination of the velocity of propagation of single-crystal silicon along a hot tin surface which has been supersaturated with silicon.

During the first quarter, laboratory apparatus was designed, built, and used to study the supercooling of Sn-Si melts and the uptake of silicon from silane. Values of the supercooling of Sn-Si melts as high as 78 °C at 1100 °C and 39 °C at 1200 °C were observed. These results were limited by nucleation caused by foreign material floating on the surface of the melt. Spontaneously nucleated planar platelet growth having growth rates of approximately 0.5 cm/min was observed at the Sn-Si supercooled surface.

Homogeneous nucleation of silane decomposition was studied at 1015 °C and 1135 °C. The flow rates of HCl required to suppress gas phase decomposition were determined for silane flow rates up to 4.5×10^{-3} mole/min. Initial silicon uptake experiments showed that at least 20% of the incoming silicon contained in a flowing silane gas stream can be incorporated into liquid tin at 1040 °C.

In the second quarter the studies of supercooling and of the interaction of silane with tin melts were continued and extended.

A horizontal boat furnace, which permits the surface scum to be blown out of the crystal nucleation zone, was built and operated. Supercooling results obtained in this apparatus are similar to those obtained earlier and appear to be limited by nucleation at

the melt-crucible surface. An electromagnetic pump was successfully incorporated into this apparatus. First examples of seeded surface growth from web-dendrite material as the nucleating seed were observed.

An experimental configuration was developed, permitting accurate measurements of the uptake of silicon from silane. Single-pass efficiencies greater than 30%, corresponding to the deposition of solid silicon at 1.8 microns/min, were measured. It was determined that silicon is incorporated into liquid tin at the same rate that it is deposited upon silicon substrates. The rate of incorporation is independent of the degree of melt saturation.

Tin melts have been driven into saturation by means of silicon input from silane and dichlorosilane. Silicon melt concentrations achieved by gas stream input were limited to the saturation value because of crystal growth nucleated by silicon deposited upon the tray walls.

The seeded growth furnace was completed and operated extensively during the third quarter. Surface growth having growth velocity as high as 5 to 6 mm/min was obtained. The surface growth generally took the form of interlocking crystals and was thin enough to follow the liquid surface. In one case its thickness was determined to be 20 microns.

A molybdenum susceptor for the seeded growth furnace was made during the third quarter. This design should eliminate the problems caused by films on the melt and seed crystal, and lead to improved crystal structure in the silicon growth.

A series of experiments was performed in order to determine whether or not the reactor gas streams were sources of contamination. Nitrogen reacts with silicon at 1100 °C to coat its surface with a film 30 Å to 150 Å thick. Silicon heated in hydrogen at temperatures between 1000 °C and 1200 °C maintains a very clean, film-free surface.

The seeded growth furnace was operated extensively during the fourth quarter. The susceptor design permits flat sheets of refractory materials to be used in making up the tray. Fused quartz and sapphire trays were used. Local surface cooling was obtained by means of a water-cooled cold finger.

Seeded surface growth was obtained in this furnace using a seed with $\langle 111 \rangle$ axis and (112) principal faces. The silicon grown out of solution had a region approximately 3 mm $\times$ 5 mm, which is substantially single-crystal with the same crystallographic orientation as the seed.

Sessile drop experiments were initiated as a rapid method of determining the suitability of various refractory materials as trays for tin melts. These experiments indicate the presence

of some impurity in the starting tin, which forms a surface film that prevents the tin from wetting silicon. This film can be removed by heating the tin to 900 °C in hydrogen.

The seeded growth furnace was operated further during the fifth quarter, using both the molybdenum and graphite susceptors. The silicon surface growth obtained from this furnace has been consistently polycrystalline. This poor growth is attributed to poisoning of the growth interface by impurities. Two impurity sources were identified, deteriorating neoprene O-rings and leaks of cooling water from the jet nozzle. The O-rings were replaced with indium gaskets, and the jet nozzle was rebuilt using hard-soldered construction. Experiments using silicon test wafers indicated that back-diffusion of air through the exit port was also taking place. Construction of a new furnace has eliminated this difficulty.

The growth habit of crystals nucleated spontaneously at the tin-silicon alloy melt surface has been studied. The crystal growth observed is consistent with dendritic and web growth from (111) singly twinned triangular nuclei. Examples of planar surface growth of small (<0.1 mm), thin crystals from these twinned surface seeds have been observed.

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Section 2

TECHNICAL DISCUSSION

A. SEEDED GROWTH FURNACE

1. Review of SGF Operation

Operation of the seeded growth furnace during the past quarter has continued to yield polycrystalline growth. Observations of the nucleation and growth of microcrystals produced during the rapid cooling of tin-silicon droplets indicated that crystal growth was being poisoned by the adsorption of impurities at the growth interface. Consequently, we devoted considerable effort to the elimination of sources of contamination. On several occasions we experienced water leaks in the cooling jet used to produce supercooling ahead of the growth region. Decomposition of neoprene O-ring seals has been eliminated by replacing them with indium gasket seals. Back-diffusion of air at the exit port has also been found to take place, necessitating a redesign of the growth furnace to increase the length of the exit port. The new furnace was recently placed in operation, and tests show that the back-diffusion problem has been eliminated.

The tray used to contain the Sn-Si alloy is another potential source of contamination. Early tests showed that quartz and boron nitride are strongly attacked by this alloy and are, therefore, unsuitable as container materials. Sapphire and alumina, on the other hand, show very little attack and appear to be satisfactory for this purpose. Tungsten has also been found to be suitable, except that the alloy tends to wet the surface and eventually creeps over the edge of the tray.

2. Tests of Furnace Cleanliness

The use of silicon test wafers to obtain a measure of the furnace cleanliness was reviewed in the Fifth Quarterly Progress Report. Additional measurements made during the past quarter are summarized in Table 1. The last column gives the results of film thickness measurements made with an ellipsometer and the visual appearance of polished silicon wafers that have been heated for 30 min at 1050 °C in the seeded growth furnace.

The 35 Å film observed in test 38A was believed to have been caused by the reaction products generated by contact between the graphite susceptor and the quartz furnace envelope. This contact was eliminated by adding platinum spacers, and the film was considerably diminished. The haze which was often found on the test wafers was found to result, in part, from inadequate cleaning procedures. After test 40B, we added an ultrasonic cleaning step before the final 10% HF etch, and this has eliminated the haze formation.

Table 1
FILM GROWTH ON SILICON TEST SAMPLES
FROM THE SEEDED GROWTH FURNACE

<u>Exp</u>	<u>Notes</u>	<u>H₂ Entry</u>	<u>H₂ Exit</u>	<u>Film Thickness and Appearance</u>
38A	1	Header	Dummy	35Å, Considerable Haze
39A	2	Header	Jet	7-9Å, Haze
40A	2	Header	Port	10-11Å, Haze
40B	2	Header	Port	6Å, Considerable Haze
41A	2	Header	Jet	3Å, Clear
42A	2	Header	Port	11Å, Clear
42B	2	Header	Port	9Å, Clear
45A	3	Header + Jet	Port	12Å, Clear
50B	4	Header	Jet	3Å, Clear
50C	4	Header + Jet	Port	3Å, Clear
50D	4	Header + Jet	Port	3Å, Clear
50F	5	Header + Jet	Port	3Å, Clear

- Notes:
- (1) Graphite susceptor in contact with quartz; jet assembly replaced by dummy header; sapphire tray; graphite ramp
 - (2) Pt spacer between susceptor and quartz
 - (3) Mo susceptor; graphite tray
 - (4) New seeded growth furnace assembly; graphite susceptor
 - (5) Sapphire tray added

With this exit port sealed and hydrogen leaving via the cooling jet line (Test 41A), a reading of 3Å was obtained, corresponding to negligible film formation. However, a significant film was observed in tests carried out with the exit port open (Tests 42A and B), indicating that back-diffusion of air was taking place. Because of these observations, we redesigned the furnace, as shown in Monthly Report No. 17. The new furnace eliminates all neoprene gaskets and has a much longer exit port, which is further extended by a quartz duct inside the furnace. Tests 50B through 50F were made using the new furnace and show no evidence for any film growth under any of the operating conditions indicated. Test 50C was conducted with the hydrogen leaving via the exit port, using the normal gas flow of 12 liters/min. The flow was reduced to 6 liters/min for test 50D, and there was still no indication of back-diffusion, so it is felt that the new design has eliminated the problem.

After these tests the furnace was loaded with tin and silicon, but the hydrogen line in the cooling jet opened up and carried water into the furnace, so the run had to be aborted. Examination disclosed that the thin-walled nickel tube that had been used to carry the cooling hydrogen had cracked as a result of thermal expansion. The cooling jet assembly is now being rebuilt with a heavier gage of stainless steel tubing for the hydrogen line.

3. Silicon Growth Experiments

Sixteen growth experiments were carried out during April and May, as described in Monthly Reports 16 and 17. These produced polycrystalline ribbons of silicon with little evidence that oriented growth had been initiated from the seed crystal. The new furnace was introduced during June, but it has not yet been operated to produce silicon.

B. VERTICAL SEEDED GROWTH FURNACE

In our seeded growth experiments we have been trying to initiate platelet growth along the free surface of a tin-silicon melt. It may turn out that the melt surface cannot be made sufficiently clean to avoid heterogeneous nucleation at this interface, or that some unrecognized instability associated with growth at the intersections of the solid, liquid, and gas phases prevents single-crystal growth from taking place. On the other hand, it might be possible to achieve seeded growth within the melt by dipping a seed crystal into a supercooled melt and drawing it up in a manner analogous to the growth of dendrite ribbons from a pure silicon melt. In this case, the floating substrate concept could be modified so that deposition from silane could be used to maintain supersaturation and to increase the thickness of the silicon to the desired value after it has emerged above the surface of the melt.

The furnace shown in Figure 1 has been constructed to explore this possibility. It consists of a quartz envelope with a graphite susceptor and alumina crucible, which will be heated with an induction coil in a hydrogen atmosphere. Tin will be placed in a quartz boat in the right arm of the furnace, melted, and allowed to pour through a small capillary into the crucible. Any surface residue that may appear as the tin melts will be skimmed off and kept in the boat by a droplet which remains in the capillary. The opposite arm of the quartz envelope will contain pellets of etched silicon, which can be pushed into the crucible by a magnetic capsule as needed during the experiment. A seed crystal will be introduced through the stainless steel header by a pull rod which is blanketed by nitrogen cover-gas to eliminate back-diffusion of air where the pull rod passes through the header. The envelope will be sealed to the header with an indium gasket.

Figure 1. Vertical Seeded Growth Furnace. The crucible is loaded with tin and silicon from the two side arms of the furnace envelope.

C. SESSILE DROP EXPERIMENTS

The observations of nucleation and growth of silicon crystals at the surface of a supercooled Sn-Si melt were extended and compared with the crystal growth produced during the operation of the seeded growth furnace. The growth mechanisms discussed in

the Fifth Quarterly Progress Report appear to be adequate to account for the crystal growth produced during the seeded experiments. Failure to achieve extended areas of single-crystal growth indicates that poisoning of the growth interface takes place after an initial period of rapid growth, which lowers the supersaturation and causes a reduction in growth velocity.

These observations stress the importance of eliminating impurities or, alternatively, of achieving growth within the melt as a means of avoiding impurities which may accumulate at the melt surface.

Section 3

TENTATIVE CONCLUSIONS AND RECOMMENDATIONS

The poor crystal structure achieved in sheet silicon grown thus far is attributed to impurities which poison the growth interface. Neoprene gaskets have been eliminated from the newly constructed seeded growth furnace, and back-diffusion of air has been prevented by a redesign of the exit port. This furnace should be operated to determine whether these changes have improved the growth conditions. Platelet growth within the tin-silicon melt should be carried out in order to determine whether or not single-crystal growth can be achieved by maintaining the growth region inside the melt instead of at the surface.

Section 4

PROJECTED ACTIVITIES

We plan to place the new seeded growth furnace in operation using inert tray materials, such as sapphire and beryllia, in order to determine whether or not the new design provides improved growth conditions. Operation of the vertical seeded growth furnace is also planned.

Appendix I

UPDATED PROGRAM PLAN

PROGRAM PLAN FLOATING SUBSTRATE PROCESS

Appendix II

MAN HOURS AND COSTS

Previous man hours were 2358 hours of scientist/engineer effort and 2509 hours of technical specialist and shop time. Total charges for the first five quarters, not including fee, were \$244,215. Sixth quarter charges to July, 1977, are 224 hours of scientist/engineer time and 134 hours of technical specialist, and shop time. Charges for this quarter, not including fee, are \$25,822. Cumulative totals for the first four quarters are 4867 man hours and \$270,037 dollar costs, not including fee.

Planned/Incurred Costs
Direct Labor Hours
Contract 954350
Began January 6, 1976

Floating Substrate Process

(Fee of \$16,875 not included)

Planned Costs - - - - -
Actual Costs - - - - -
Planned Hours - - - - -
Actual Hours

	This Month	Total To Date
Costs	\$25,822	\$270,037
Hours	358	5,225