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

Fifth Quarterly Progress Report, January 1, 1977—April 1, 1977

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April 12, 1977

MASTER

Work Performed Under Contract NAS-7-100-954350

General Electric Company
Schenectady, New York

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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\$6.00 (foreign)
Microfiche \$3.00 (domestic)
\$4.50 (foreign)

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Fifth Quarterly Progress Report

Subcontract No. 954350

by

M. Garfinkel, Program Manager
R. N. Hall, Principal Investigator

Period Covered: January 1, 1977 to April 1, 1977

April 12, 1977

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays

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ABSTRACT

The seeded growth furnace with the slotted molybdenum susceptor has been operated during the past quarter. Flat sheets of sapphire were used as the tray, and local cooling at the tin-silicon alloy surface was provided by a symmetric water-cooled jet.

The silicon surface growth obtained during the past quarter has been consistently polycrystalline. This poor growth is attributed to impurities in the seeded growth furnace, caused by leakage into the system. Two sources have been identified: deteriorating neoprene O-rings and leaks of cooling water from the jet nozzle. The O-rings were replaced with indium gaskets, and the nozzle is being rebuilt.

Weight loss measurements of the sapphire tray plates indicate that they suffer negligible attack by tin-silicon alloy melts at 1000 ° to 1100 °C.

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 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 is well known and presents no problems, the current effort will focus upon the nucleation and rapid growth of substrate silicon from supercooled melts. We will perform studies of (1) supercooling, (2) crystal growth from a 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 5-6 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 slotted molybdenum susceptor was used 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 x 5 mm, which is substantially single-crystal with the same crystallographic orientation as the seed.

Sessile drop experiments were initiated in the fourth quarter 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.

Section 2

TECHNICAL DISCUSSION

A. SEEDED GROWTH FURNACE

1. Review of SGF Operation

The initial operation of the seeded growth furnace was carried out with a graphite susceptor, and with local cooling produced by means of a gas jet which was directed upon the surface of the melt near the growth region. This configuration was used through run SGF-15, and produced encouraging silicon growth, at rates up to 5 mm/min, but which showed very poor crystal structure. Failure to achieve good crystal growth was attributed to contamination resulting from back-diffusion of air through the exit port and around the cooling jet opening, possible overheating of the cooling jet itself, reaction between the quartz tray and the Sn-Si melt, and gas evolution from the graphite from which the susceptor was constructed. The use of nitrogen-hydrogen mixtures for the furnace atmosphere was also suspected of contributing to nitride film formation on the surface of the melt.

A number of changes were introduced at run SGF-16 in order to correct these problems. The graphite susceptor was replaced with a slotted molybdenum susceptor in order to eliminate possible out-gassing and to permit the use of inert tray materials such as sapphire or beryllia. A water-cooled cold finger was used with a pure hydrogen atmosphere to provide local cooling, and a duct was added at the exit port to reduce back diffusion into the furnace. These changes caused a distinct improvement in furnace cleanliness as evidenced by reduced film formation on the melt surface. The growth achieved in run SGF-17 was particularly encouraging, as shown in Figure 1 of Monthly Report No. 10. However, visibility was greatly restricted by the cold finger, making it very difficult to observe and control the growth region, so the method of cooling was changed back to a gas jet, this time using a water-cooled nozzle in order to prevent overheating and to achieve maximum local cooling.

Operation during the past quarter (January through March) has continued to yield polycrystalline growth. A leak in the gas jet assembly was corrected after run SGF-23, and a number of furnace modifications have been introduced in order to eliminate suspected sources of contamination. In addition to silicon growth experiments we have been evaluating the furnace cleanliness using test wafers and have been studying the nucleation and growth of crystals formed on the surface of rapidly cooled Sn-Si droplets in order to gain a better understanding of the growth mechanisms and of the phenomena which terminate the growth of crystal platelets.

2. Tests of Furnace Cleanliness

Experiments described in the Third Quarterly Progress Report showed that silicon test wafers heated in a clean hydrogen atmosphere for an hour at 1070 °C would show only a few angstroms of surface film as measured with an ellipsometer. Thicker films or spotted and hazy surface appearance was indicative of a contaminated atmosphere. Examples of such tests carried out in the Seeded Growth Furnace were reported in Table I of the Fourth Quarterly Progress Report. In only two of these tests, SGF-14C and 14D, were clean conditions indicated, as evidenced by film thicknesses of 7.5 and 6 Å, respectively.

The results of similar tests carried out during the past quarter are summarized in Table I. The test wafer from run SGF-22A appeared to have a bright, clean surface, but the ellipsometer showed that a 20 Å film was present. Subsequent to this experiment, a leak in the cooling jet assembly was corrected and improvements in gas ducting were made at the exit port. Several growth experiments were carried out before tests of the furnace cleanliness were resumed. Tests 30A and B showed staining of the test wafer. The neoprene O-rings at the ends of the furnace tube were changed to Teflon for experiments 31A and B. These wafers came out free of stains but showed a high index film. Since then we have been using indium gaskets, and the staining problem has been largely eliminated. The stains noted on many of the recent test wafers are attributed to an accident which occurred during SGF-32, in which the susceptor became coated with tin which was not entirely removed by the cleanup procedure. These later tests still show significantly more film growth than should have taken place in a clean system. The final test, SGF-37, was carried out with a graphite susceptor and a dummy header in which the jet assembly was eliminated. Only a very thin film, 5 Å, was indicated by the ellipsometer measurement, and it was concluded that a small leak must still have been present in the cooling jet. A new cooling jet with hard solder joints has been built, and growth experiments will be resumed after it is verified that clean conditions can be achieved.

3. Silicon Growth Experiments

Numerous growth experiments were carried out in the Seeded Growth Furnace during January and February, as described in Monthly Reports 13 and 14. These continued to yield polycrystalline material and efforts to eliminate possible sources of contamination were intensified. In addition to the measures described above, we closed several header holes that had been used to pass the thermocouple leads and other structural members, leaving only the exit port. Run SGF-35 was carried out after these modifications but had to be terminated because a droplet of tin made contact with the susceptor and began to spread over its surface. In view of the repeated difficulties that we have had with tin making contact with the molybdenum susceptor, we plan to reevaluate the suitability of graphite as a susceptor material. Earlier tests showed no evidence for film growth on silicon test

Table I

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>
22A	1	Jet	Port	20 Å, clear
30A	2	Header + Jet	Port	Haze, no measurement
30B		Header	Port	Haze, no measurement
31A	3	Header	Port	Clear, high index film
31B		Jet	Port	Clear, high index film
32B	4	Header	Port	12 Å, clear
32C		Jet	Port	16 Å, clear
32D	5	Jet	Port	13 Å, clear
33B	5	Header	Port	15 Å, haze at edges
33C	5	Header	Port	7.5 Å, haze at edges
34B	6	Header	Jet	14 Å, haze at edges
34C	6	Jet	Header	12 Å, faint haze
34D	6	Header	None	17 Å, clear
36B	7	Header	Jet	16 Å, clear
37	8	Header	Dummy	5 Å, faint haze at one end

Notes: (1) No susceptor, sapphire tray, water leak in tray not corrected
 (2) Leak fixed, exit port extended, quartz duct added
 (3) TeflonTM gaskets at ends of furnace tube
 (4) Indium gaskets introduced
 (5) Exit port partly blocked
 (6) Header holes sealed; exit sealed
 (7) Graphite susceptor
 (8) Jet assembly replaced by dummy header

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wafers heated with graphite susceptors, and these results are substantiated by experiment SGF-37, shown in Table I, in which a graphite susceptor was used. Returning to the use of graphite for this purpose would eliminate many of the operational difficulties that we have encountered with the seeded growth furnace.

B. SESSILE DROP EXPERIMENTS*

The nucleation and growth of silicon crystals on the surface of super-cooled tin-silicon alloy melts has been studied during the past quarter. The procedure followed was (1) to heat a drop of tin supported by a silicon wafer to a temperature between 900 ° and 950 °C, (2) allow it to stand long enough for saturation to take place, and (3) to then quench the system by dropping the R-F heating power to zero.

Many planar shapes were observed. A detailed analysis of these shapes suggests that the primitive seed, formed under conditions of the initial large supersaturation, has the form of a singly twinned triangular nucleus. The twin plane is (111) and the vertex angles of the triangle are in the $[\bar{1}\bar{1}2]$, $[2\bar{1}\bar{1}]$, and the $[\bar{1}2\bar{1}]$ directions. The seed has only one twin plane and grows to an initially closed triangular shape characterized by a ridge extending completely around its median plane. The triangles grow very slowly thereafter, since there is no reentrant to act as an efficient nucleation site.

In most cases continued crystal growth proceeded by the growth of linear dendritic leaders out from the vertices of the completed triangle along the coplanar system of $\langle 110 \rangle$ directions and by the subsequent growth of planar web from the reentrant sides of these dendritic leaders. Examples illustrating various aspects of this type of surface growth were presented in Monthly Report Number 14, including an example of the growth of a uniform plane parallel plate within the 60 ° angle defined by the reentrant edges of two $\langle 110 \rangle$ dendrites.

Another type of crystal growth was observed to take place, namely the filling in of the acute angle between the dendrite arms extending from the completed vertices of the triangular nuclei. Crystals in which this type of growth has occurred are shown in Figures 1 and 2.

The basic process is shown occurring at the A and B corners of the nucleus in Figure 1. The triangular units AJD and BEF have outward facing reentrants, which will facilitate two-dimensional growth in the absence of adsorbed contamination. A slowing down of outward growth possibly resulting from an exhaustion of the supply of silicon atoms and associated development of contamination is followed by an increase in supersaturation at E and F and the development of the dendritic leaders with outward facing ridges along ED and FG.

*The crystallographic analysis was performed by Prof. J. W. Mitchell.

Figure 1. Crystal Exhibiting Planar Growth in a $\langle \bar{1}12 \rangle$ Direction, Nucleated by a Re-entrant Twin Pair

Figure 2. Crystal Showing Many Aspects of Surface Growth

The crystal of Figure 2 illustrates many of the growth features previously described in Monthly Report Number 14, as well as several significant new features. It thus provides a convenient summary. The acute angle at the vertex at B has filled in via the planar growth process just described. It has developed 120° angles at E and F, as shown in Figure 1. The slow outward growth at the centers of the ridges defining the exterior edges of the triangular nucleus is quite evident.

There are six areas of web growth which are of interest. The planar growth in area 1 at the corner B has already been discussed. Area 2 is developing outside the dendritic leaders which defined the ED edge parallel to BA by the motion of a reentrant edge towards D, as shown in Figure 3. Areas 3 and 4 are developing by the motion of the inner reentrant edges, parallel initially to BA and AC towards BA and AC. The relative rates of outward motion of the ridges and inward motion of the reentrants under the influence of the same flux of silicon atoms clearly establish the relative two-dimensional nucleation efficiencies of ridges and reentrants. This observation also suggests that screw dislocations in the twinning plane are not playing any significant role if they are indeed present. Finally, the areas at 5 and 6 show the growth of web in the net direction of an outward ridge bridging two reentrants by the growth of those reentrants toward each other.

Figure 3. Planar Growth of a Reentrant Edge

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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. Further measures to detect and eliminate such contamination are being undertaken.

The preferred surface growth habit of heavily supercooled tin-silicon alloy melts saturated at 900 ° to 950 °C appears to be the nucleation of (111) twinned triangular nuclei and their extension by means of planar growth along $\langle 1\bar{1}2 \rangle$ directions, and linear dendritic growth along the $\langle 110 \rangle$ directions. Thin surface webs grow out from the reentrant edges of the $\langle 110 \rangle$ dendrites.

Section 4

PROJECTED ACTIVITIES

Stringent tests of the cleanliness of the furnace atmosphere will be carried out using silicon test wafers and measurements of the purity of the gas exiting through the exit port. Susceptors made from graphite and molybdenum will be evaluated by these tests and by the results achieved in sheet growth experiments using them.

We will continue the study of the growth habit of silicon at the surface of the sessile drop. The effects of supercooling upon linear and planar growth will be investigated.

Appendix I

UPDATED PROGRAM PLAN

PROGRAM PLAN FLOATING SUBSTRATE PROCESS

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Appendix II

MAN HOURS AND COSTS

Previous man hours were 2060 hours of scientist/engineer effort and 2352 hours of technical specialist and shop time. Total charges for the first four quarters, not including fee, were \$210,369. Fifth quarter charges to April, 1977, are 298 hours of scientist/engineer time and 157 hours of technical specialist, and shop time. Charges for this quarter, not including fee, are \$33,846. Cumulative totals for the first four quarters are 4867 man hours and \$244,215 dollar costs, not including fee.

Planned/Incurred Costs
Direct Labor Hours
Contract 954350
Began January 5, 1976

Floating Substrate Process

Planned Costs o--o--o--
Actual Costs —————
Planned Hours - - - - -
Actual Hours

	This Quarter	Total To Date
Costs	\$33,846	\$244,215
Hours	455	4,867