MASTER

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

Fourth Quarterly Progress Report,
September 27, 1976—December 31, 1976

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R. N. Hall

January 7, 1977

Work Performed Under Contract No. NAS-7-100-954350

General Electric Company
Schenectady, New York

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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Fourth Quarterly Progress Report
Subcontract No. 954350

by

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R.N. Hall, Principal Investigator

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Period Covered: September 27, 1976 to December 31, 1976

January 7, 1977

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ABSTRACT

The seeded growth furnace with a slotted molybdenum susceptor has been operated during the past 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 has been obtained in this furnace using a seed with $\langle 111 \rangle$ axis and (112) principal faces. The silicon grown out of solution has a region approximately 3 mm x 5 mm, which is substantially single-crystal with the same crystallographic orientation as the seed.

Sessile drop experiments have been 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.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1
2 TECHNICAL DISCUSSION	3
A. Seeded Growth Furnace	3
1. Operation with Molybdenum Susceptor	3
2. Furnace Cleanliness Tests	4
B. Sessile Drop Experiments	5
C. Problems	7
3 TENTATIVE CONCLUSIONS AND RECOMMENDATIONS.	8
4 PROJECTED ACTIVITIES	9
5 NEW TECHNOLOGY	10
Appendix I -- UPDATED PROGRAM PLAN	11
Appendix II -- MAN HOURS AND COSTS.	12

LIST OF ILLUSTRATIONS

<u>Figure</u>		
1 SEM photograph of surface film on a tin drop heated to 500 °C		6
2 SEM photograph of the surface of a tin drop heated to 800 °C		6
3 Profile view of a 2 mm tin drop		7

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.

Section 2

TECHNICAL DISCUSSION

A. SEEDED GROWTH FURNACE

1. Operation with Molybdenum Susceptor

A graphite susceptor was used in our initial work with the seeded growth furnace. The experiments showed that surface growth of silicon could be achieved, but the crystal structure was not satisfactory. The poor crystal growth was believed to be caused by some form of furnace contamination, so the furnace was reconstructed with materials which were expected to yield a much cleaner growth environment. The susceptor was changed to molybdenum and designed so that the tray could be made from various inert materials such as quartz, boron nitride, sapphire, or beryllia. We also introduced, in place of the gas jet used previously, a water-cooled cold finger as a means of producing local cooling near the growth region. The seeded growth experiments which followed this change were accompanied by test experiments to evaluate the cleanliness of the growth chamber. The results of these tests will be summarized in a later section of this report.

The molybdenum susceptor was first heated alone in the furnace to 1140 °C in hydrogen to clean it up. A quartz tray was added, and the furnace was again brought to the operating temperature as part of the initial testing program. Two silicon test wafers were then run in order to obtain a measure of the cleanliness of the furnace. These experiments, SGF-15C and SGF-15D, resulted in slight film growth, as shown in Table 1 (17 and 19 Å, respectively), indicative of reasonably clean furnace conditions.

Table 1

FILM GROWTH ON SILICON TEST SAMPLES FROM THE SEEDED GROWTH FURNACE

Exp.	Temp (°C)	Time (min)	H ₂ Flow (ℓ/min)	t (Å)	Index	Comments
14A*	1070	45	10	463	3.13	Hazy, non-specular
14B*	1070	45	8	385	1.50	
14C*	1070	45	10	7.5	—	
14D*	1070	45	10	6	—	
15C	1070	55	6	17	—	
15D	1080	50	6	19	—	
18A	~1000	15	5	16.8	—	Clear surface
18B	1130	15	5	301	1.91	Haze, a few spots
19A	1075	30	6	130	3.5	Spots at one end
19B	1072	30	10	195	2.56	Haze, many spots
20A	1120	30	5	37	—	Clear surface
21A	1070	30	6	14	—	Haze
21B	1080	30	6	—	—	Heavy haze, spots

*These results were obtained with the graphite susceptor and were reported earlier in the Third Quarterly Progress Report.

We next added a charge of Sn and Si and attempted to grow some silicon in experiment SGF-16. With the use of the water-cooled cold finger, visibility was poor, and only a slight amount of growth was obtained before it was discovered that tin was draining out of the tray, a condition requiring that the run be terminated.

The susceptor was cleaned, vacuum fired to 1700 °C, and then reassembled with a sapphire tray, after a minor modification to prevent tin from contacting the susceptor. It was heated empty and then heated several times using pure tin. The system appeared very clean, and there was no evidence of fluff formation like that always observed when quartz is used to contain the tin. Silicon was added, and some sheet growth was produced in SGF-17A and SGF-17B. Conditions were not favorable because of the poor visibility caused by the cold-finger, but nevertheless some regions of single-crystal growth having the same orientation as the seed were obtained, as reported in Monthly Report No. 10. Some leakage of tin occurred again, by creepage along the tungsten wire used for electromagnetic stirring, an occurrence requiring that the susceptor be cleaned and vacuum fired again.

The cold finger was replaced with a water-cooled gas jet, and the furnace was reassembled with a sapphire tray but without the tungsten electrode, and some test wafers were run. In SGF-18A the test wafer was heated only to 1000 °C for 15 minutes, and it came out with a clear surface and a 16.8 Å film thickness, as indicated by ellipsometry. However, a second wafer run at 1130 °C showed a hazy surface and several spots; the measurements indicated a 300 Å film.

In view of this heavy deposit, the system was opened up so the gas jet assembly could be leak tested. It was found to be tight, so two more tests were carried out, SGF-19A and SGF-19B. Because both tests indicated rather heavy deposits, the furnace was opened and reexamined. There appeared to be evidence of some residual tin or a tin-molybdenum compound on the susceptor. As a result, the furnace was grit-blasted, cleaned, and vacuum fired again. The next test wafer, SFG-20A, came out considerably better. It was free of haze or spots and showed only a 37 Å film.

In SFG-20B tin was added and heated to 1000 °C. The surface remained bright and clear, so Si was added and the system was brought to the solution temperature of 1180 °C. At this point it was noticed that a deposit could already be seen on the surface of the seed crystal, which had previously been placed on the boron nitride slide leading to the exit port. By the time the seed was fed into the melt, this deposit had become so thick that it caused some difficulty in joining the seed to the melt. A few centimeters of silicon were grown, but the silicon was of poor quality. It is clear that a serious contamination problem, which must be tracked down and eliminated, remains.

2. Furnace Cleanliness Tests

Silicon test wafers were used to obtain an indication of the cleanliness of the furnace, as described in the Third Quarterly Progress Report. Etch-polished wafers were stripped of oxide and heated in the seeded growth furnace for a half hour or so and then measured with an ellipsometer to detect the presence of any film that had formed on the surface of the wafer. Under clean furnace conditions this test typically yielded readings of ~4 Å after heating for 45 minutes at 1070 °C in hydrogen.

Table 1 summarizes the results of such tests conducted in the seeded growth furnace. The experiments were given successive numbers each time the furnace was assembled for operation. Once assembled, the furnace could be heated several times to

carry out cleanliness tests or to grow silicon, and these experiments were distinguished by the letters A, B, C, etc. The molybdenum susceptor was used for the first time in Run 15.

The thickness of the films observed indicates that the furnace was not being operated under clean conditions. The water-cooled gas jet was carefully tested twice by means of a helium leak detector, but no evidence for a leak could be found. Some film formation might have resulted from the Sn-Mo residue left after the leaks, which took place during experiments 16 and 17, but the susceptor has been cleaned and vacuum fired several times since then and should now be free of this residue.

It now appears most likely that the film growth observed has often been caused by back-diffusion of air through the exit port. This view is supported by observations made during SGF-20B. In this experiment the tin-silicon melt remained bright and clear in appearance until the seed crystal was introduced through the exit port. Then a heavy deposit, which became thick enough to interfere with the splicing operation, began forming on the seed. This behavior suggests that a reverse flow pattern may be set up by the introduction of the seed, causing air to stream back into the furnace and generating oxides of Si, Sn, and/or Mo. The seed from this experiment is being studied by X-ray emission microscopy to determine the composition of the deposit. The exit port has been extended in order to reduce the possibility of back-diffusion in future experiments.

B. SESSILE DROP EXPERIMENTS

An extensive series of sessile drop experiments designed to determine the compatibility of various tray materials with tin-silicon alloy melts was performed during the past quarter. These experiments consisted of melting a drop of tin or tin-silicon alloy upon a substrate of the material in question and the careful observation of the surface of the molten drop. Any scum or film which forms through interaction of the liquid metal with the substrate (because of impurities in the starting tin or for any other reason) will float to the surface of the drop, where, because of the specular nature of the liquid surface, it is highly visible. The ability of any proposed tray material to maintain a clean melt surface may be quickly and conveniently checked in this manner.

The sessile drop experiments were performed under a wide variety of experimental conditions. Substrate materials included float-zone silicon, Czochralski-grown silicon, sapphire, and spinel; silicon, graphite, and silicon sealed graphite susceptors were used; and experiments were performed both in hydrogen and in vacuum. Specific details are given in Monthly Reports 10 and 11.

Apart from minor details, the behavior of the tin drop under these varied conditions was quite consistent. A thin film covering the surface of the tin drop was always observed shortly after the tin had melted. The film maintained its coherence up to some intermediate temperature (700°C - 850°C), at which point it began to break up. Upon further heating the film continued to disintegrate until at 900°C it disappeared completely or coalesced into several small scum patches. The surface of the tin was then clean and bright.

Figure 1 is a SEM photograph of the surface of a tin drop that was supported by a float-zone silicon substrate and heated in hydrogen to 500°C . The film is clearly shown by the speckled appearance of the surface. The cracks in the film (the clear dark areas) are probably the result of differential thermal contraction of the film and the tin drop.

Figure 2 is another SEM photograph of the surface of a tin drop heated to 800°C on silicon. The film in this case is at the stage where it is partially broken up. The surface

Figure 1. SEM photograph of surface film on a tin drop heated to 500 °C

Figure 2. SEM photograph of the surface of a tin drop heated to 800 °C

film, which initially completely covered the tin surface, as in Figure 1, has changed to an open, lacy structure, and large, open patches of clean tin are clearly visible. The dark triangular or hexagonal areas are silicon platelets that regrew upon the drop surface.

This film interferes with the wetting of clean silicon by tin. While we occasionally observed local, spotty wetting of silicon substrates by the sessile drop at temperatures as low as 500 °C, consistently low contact angles could not be obtained until the tin had been heated to 900 °C in order to remove the film. Figure 3 is a SEM view of a 2 mm tin drop that was melted upon a float-zone silicon substrate and heated to 600 °C. An especially thick portion of the film is evident at the center and across the left side of the drop. The poor wetting is shown clearly by the contact angle, which is greater than 90°.

Figure 3. Profile view of a 2 mm tin drop

Electron beam excited X-ray fluorescence examination of this specimen showed only silicon and tin. The film thus does not contain any heavy metals. This technique, however, is insensitive to elements with Z less than that of silicon and can thus not indicate the presence of oxides, nitrides, or carbides. Auger spectroscopy will be used to identify the film.

The appearance of a film on the surface of the tin drop independent of substrate indicates that the impurity causing the film is present as a contaminant in the tin itself. While it is desirable to eliminate this impurity completely, our experience with silicon and sapphire substrates shows that this is not essential. The consistent disappearance of the surface film at 900 °C shows this and is clear evidence that clean alloy melt surfaces may be obtained and maintained in practical systems.

C. PROBLEMS

The seeded growth furnace has been experiencing difficulties because of a contaminant that forms deposits on the seed crystal and interferes with the growth process. This problem appears to be caused by back-streaming of traces of air into the exit port. This port has been extended by adding a duct, which should prevent this back-streaming and filming in future experiments.

Section 3

TENTATIVE CONCLUSIONS AND RECOMMENDATIONS

We plan to continue the operation of the seeded growth furnace using sapphire and beryllia trays in a hydrogen atmosphere, with the water-cooled gas jet to provide local cooling in the growth region.

There is an impurity present in our starting tin, which forms a thin film upon the melt surface. It is, nevertheless, possible to remove this film and to obtain clean melt surfaces by heating the tin to 900 °C in hydrogen.

We plan to continue the sessile drop experiments using beryllia and graphite as substrates.

Section 4

PROJECTED ACTIVITIES

The major focus of our efforts for the next period will be on surface growth.

We plan to continue working with the seeded growth factor in order to determine the growth conditions that are most favorable for rapid surface growth. The new molybdenum susceptor version of this furnace is completed and will be operated with various tray materials under what are expected to be much cleaner growth conditions.

Sapphire and beryllia trays will be used. The local cooling required for surface growth will be supplied by a symmetric gas jet.

Section 5

NEW TECHNOLOGY

There are no reportable items of new technology.

Appendix I

UPDATED PROGRAM PLAN

PROGRAM PLAN FLOATING SUBSTRATE PROCESS

Appendix II

MAN HOURS AND COSTS

Previous man hours were 1606 hours of scientist/engineer effort and 1997 hours of technical specialist and shop time. Total charges for the first three quarters, not including fee, were \$164,240. Fourth quarter charges to Dec. 31, 1976 are 454 hours of scientist/engineer time and 355 hours of technical specialist, and shop time. Charges for this quarter, not including fee, are \$46,129. Cumulative totals for the first four quarters are 4412 man hours and \$210,369 dollar costs, not including fee.

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

Floating Substrate Process

	This Quarter	Total To Date
Planned Costs		
Actual Costs		
Planned Hours		
Actual Hours		
Costs	\$46,129	\$210,369
Hours	809	4,412