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FLOATING SUBSTRATE PROCESS

First Quarterly Progress Report, January 6, 1976—March 28, 1976

R. N. Hall

MASTER

April 2, 1976

Work Performed Under Subcontract No. JPL 954350

General Electric Company
Schenectady, New York

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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FLOATING SUBSTRATE PROCESS

Large Area Silicon Sheet Task
Low-Cost Silicon Solar Array Project

First Quarterly Progress Report

Period Covered: January 6, 1976 to March 28, 1976

by

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

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April 2, 1976

Subcontract No. 954350

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ABSTRACT

Laboratory apparatus has been designed, built, and put into operation to study the supercooling of Sn-Si melts and the uptake of silicon from silanes. Values of supercooling of Sn-Si melts as high as 78 C at 1100 C and 39 C at 1200 C have been observed. Results to date have been limited by nucleation caused by foreign material floating on the surface of the melt. Spontaneously nucleated planar platelet growth has been observed at the Sn-Si supercooled surface having growth rates of approximately 0.5 cm/min.

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

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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 in the 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 cm^2 area and the determination of the velocity of propagation of single crystal silicon along a hot tin surface which has been supersaturated with silicon.

The vertical furnace for the study of supercooling is shown in Figure 1. This apparatus has been built, assembled, and extensively operated during the past reporting period. A crucible containing a Sn-Si alloy is heated in an isothermal enclosure under a hydrogen and/or nitrogen atmosphere until all the silicon has dissolved. At this point, the temperature is measured, and an optical pyrometer reading is taken of the surface in order to determine the emissivity correction of the liquid. A jet of cold hydrogen is then directed upon the center of the alloy as indicated in Figure 1, in order to reduce the temperature of this portion of the liquid. The decrease in temperature is followed by means of optical pyrometer measurements, and the value at which crystals begin to form on the surface of the liquid indicates the amount of supercooling that is achieved.

We have already determined, in work performed prior to the current contract effort, that silicon is taken up by liquid tin from an impinging silane gas stream. These experiments will be extended in a systematic way in order to determine the rates of silicon uptake as a function of the solute and gas stream concentrations, and to determine the degree of supersaturation that may be achieved and whether it is limited by the formation of silicon nuclei at the surface of the alloy. This information is basic in determining the balance between the two methods of supplying silicon to the growing edge of

Figure 1. Vertical Furnace for Supercooling Studies

the silicon sheet -- either directly from the incoming gas stream, or by means of mass flow of the alloy from a region where it has been brought to saturation at a higher temperature.

The apparatus used in this experiment is shown in Figure 2. It consists of a shallow horizontal quartz tray containing the tin charge, which is in thermal contact with an rf heated graphite susceptor. The reactor is water-cooled to prevent silicon depletion from the incoming silane-bearing gas stream and to prevent silicon from being deposited upon the inner surface of the quartz tube. The melt temperature is determined by means of optical pyrometer measurements of the graphite susceptor. The gas stream is designed for "forced laminar flow" so that there is a well defined gas velocity and interaction length.

The experimental procedure will be to heat the charge to a fixed temperature, expose it to the gas mixture for a fixed time, quench it to room temperature, and weight it. This procedure will be repeated as required. The incorporation of silicon from the gas into the liquid is given directly by the change in weight--the loss of tin being negligible at the temperatures of interest. Measurements will be made at various silane concentration and alloy temperatures. The onset of surface nucleation will be determined visually.

Figure 2. Horizontal Reactor for Silicon Uptake

The experiments at high silane gas concentrations and at high liquid saturations will be repeated with the addition of HCl to the incoming gas stream. This will be done in order to determine the extent to which homogeneous gas phase nucleation and critical nucleus formation in the super-saturated liquid can be suppressed.

Section 2

TECHNICAL DISCUSSION

SUPERCOOLING

TIN CLEANING AND PREPARATION

High purity tin obtained from Kawecki Berylco Industries has been used in most of our experiments. This is obtained in the form of 1200 gram billets and is designated 5N5 purity (99.9995 percent). The chemical analysis supplied by the vendor is tabulated below:

Chemical Analysis, ppm

Cu	-	1.6
Fe	-	0.09
Cl	-	0.29
S	-	0.81
Pb	-	0.17
As	-	0.02

Other elements are beyond detection.

Charges of the desired size are cut off with a saw and etched clean using a 1-1-1 etch which consists of equal parts of HF, HNO₃, and H₂SO₄. It is then melted under an atmosphere of H₂ or N₂ and poured through a capillary funnel into a casting mold to produce an ingot of the required form and weight, as described in Monthly Report No. 2. A properly cleaned melt will show no evidence of any dust or film when examined in a darkened room using a microscope lamp to illuminate its surface.

Quartz or pyrex make suitable molds except that the tin often sticks, causing them to break during cooling. Molds machined from extruded BN have been found to leave a faint film on the surface of the tin. Vacuum fired graphite molds leave a film of graphite dust on the surface of the tin until they have been broken in by repeated use. They eventually clean up and yield ingots which appear to be completely free of any surface contaminant. Pyrolytic BN would probably be even more suitable but crucibles of the proper size have not yet been obtained.

CRUCIBLE MATERIALS

In conducting the supercooling experiments we have worked with crucibles made of fused quartz, BN, alumina, and graphite. So far, BN and alumina appear most suitable as containers for the Sn-Si alloy.

Fused quartz is attacked to some extent by hot tin. When a pure tin charge is heated for the first time to 1200 C in quartz under a hydrogen atmosphere, the surface appears bright and clean except for a small patch of scum which generally gathers together and floats near the center of the melt. However, if the tin is cooled and then reheated, one observes that a thin transparent film lifts off from the surface of the melt and gathers together into a tenuous "fluff ball." X-ray and chemical analyses of the fluff have shown that it is SiO_2 with particles of metallic tin. This fluff formation occurs repeatedly each time the tin is cooled again and reheated in quartz, but has not been observed when other crucible materials were used.

BN appears quite promising for this purpose. Extruded BN contains considerable B_2O_3 and other impurities and results in considerable scum accumulation on the surface of the melt. On the other hand, pyrolytic BN ("Boralloy" crucibles obtained from Union Carbide Corporation) is much cleaner and appears to undergo little reaction with the melt. Furthermore, there is no adhesion between the crucible and its charge when the system is cooled to room temperature.

Morganite alumina crucibles also appear to be quite nonreactive and leave only a small amount of scum on the melt surface. They have the practical disadvantage of sticking firmly to the solidified charge after the system has been cooled.

Graphite behaves nicely with pure tin, but when silicon is added the melt wets the crucible and forms a firm bond upon cooling. It may be possible to solve this difficulty by coating the graphite with a layer of SiC.

TEMPERATURE MEASUREMENT

It is often convenient to measure the temperature of the Sn-Si alloy by optical pyrometer measurements of the free surface of the liquid alloy. Further measurements have confirmed our previous determination of 0.28 for the spectral emissivity of this alloy at 0.65μ in the temperature range 1100 to 1200 C, as reported in Monthly Report No. 2.

SUPERCOOLING RESULTS

The KB series of supercooling experiments has now been extended through run 19. Several kinds of crucibles were used as described above, and tests were conducted using Si/Sn weight ratios chosen to give solution temperatures near 1100 and 1200 C respectively. The values of supercooling measured during these experiments are plotted in Figure 3. Point "6-9" represents the average value obtained during runs 6 through 9. The two values for run 16 were obtained using different positions of the cooling gas jet and flow velocities. More supercooling was obtained with large flow rates and with the jet close to the surface of the liquid. After run 17 was completed, the charge

was removed for examination and then replaced and rerun with the upper heat shield removed to give "17 Remelted."

Figure 3. Supercooling vs Si/Sn Weight Ratio.
The cluster of points near ratios of 0.016 corresponds to 1100 C, and that near 0.035 corresponds to 1200 C.

There is considerable scatter among the various ΔT values, much of which can be attributed to the use of different gas flow rates and H_2/N_2 ratios, as well as to different positions of the inlet tube. Nevertheless, a clear trend toward less supercooling is evident with increasing silicon content. This trend is consistent with observations reported in other alloy systems.

The supercooling results that we have obtained so far have been the result of nucleation by the scum floating on the surface of the melt. Greater supercooling will presumably result when the scum is eliminated. We regard the values obtained so far as encouraging, since they are in the same range as the values assumed in the analysis presented in the contract proposal, Section 1 -- Technical.

CRYSTAL GROWTH

In the supercooling experiments, crystals are first observed at the edge of the scum which is blown away from the center of the melt by the gas jet. They grow more or less toward the center of the melt, usually in the form of branching needles. This type of multiply branched crystal growth is shown in Figure 4.

Figure 4. Typical Example of Multiply Branched Dendritic Growth

On several occasions, however, silicon crystals have grown in the form of platelets floating on the surface of the supercooled melt. Examples are shown in Figures 5 and 6. These crystals appeared to be nucleated at the edge of the scum at their sharp corner. They were observed to grow in length to the "dagger" shapes shown at the rate of about 1 mm in 10 seconds.

The platelet growth shown in Figures 5 and 6 is very encouraging, since it demonstrates that silicon crystals can be rapidly grown on the melt surface in the form of two-dimensional plates rather than the fern-like dendritic needles that are more commonly formed during the solidification of alloys.

SILICON UPTAKE INTO TIN

HOMOGENEOUS NUCLEATION

A series of experiments, designated H8 and H9, have been performed to determine the flow rates of HCl necessary to suppress homogeneous gas

Figure 5. Example of Two-Dimensional Planar Growth. The dagger shaped crystal grew by itself. The branched dendritic crystals surrounding it developed separately at a later stage of the cooling cycle

Figure 6. Several Examples of Planar Growth

phase decomposition of SiH_4 . The apparatus used was the horizontal system described above. Gas mixtures of H_2 , N_2 , SiH_4 , and HCl were passed over a heated graphite susceptor. The temperature was measured with an optical pyrometer. The sightings were taken into a hole drilled into the graphite so no emissivity corrections were required.

The presence of gas phase decomposition of the incoming SiH_4 was determined visually. The region above the susceptor was illuminated by an intense beam of light incident from above. Solid silicon particles in the gas stream were easily seen by the light that they scattered out of this beam. Our procedure was to set the desired flows of H_2 , N_2 and SiH_4 with the HCl flow initially at zero. Under these conditions, with exceptions to be discussed below, silicon "smoke" was formed in the gas stream. The flow of HCl was then increased until the formation of this "smoke" was totally suppressed. The HCl flow rate was cycled through this value several times in order to verify the result.

When homogeneous nucleation occurred, silicon particles were observed in a narrow band less than one millimeter wide located approximately five millimeters above the hot graphite surface. This band of "smoke" was planar indicating that the gas flow in the hot zone was laminar. High sensitivity in the detection of the onset of homogeneous gas phase nucleation was achieved by sighting along this plane. HCl flow rates were determined to a precision of 5 cc/min and the SiH_4 rates are accurate to 0.7 cc/min. All flow meters used were individually calibrated against a Brooks Model 1055 Gas Flow Calibrator.

Measurements were made at 1015 C and at 1135 C for hydrogen flows of 900 cc/min and 2000 cc/min. Two concentrations were run since hydrogen was expected to inhibit the decomposition of silane via the reaction

The flow of N_2 was in all cases kept constant at 1200 cc/min.

For each set of experimental conditions there was a threshold SiH_4 flow rate below which there was no homogeneous nucleation even without any HCl . These were 14.7 cc/min and 33.5 cc/min for the low and high H_2 flow rates at 1015 C, and 4.2 cc/min and 11.6 cc/min at 1135 C. The results obtained are presented in Figure 7.

Each curve marks the boundary separating the regime of homogeneous gas phase decomposition from that where essentially all the silicon that is extracted from the gas stream is deposited upon the hot susceptor. The region generally above and to the left of these curves represents, of course, the gas flow conditions under which we will perform the silicon uptake experiments.

Figure 7. Boundary Lines for Homogeneous Gas Phase Nucleation of Silicon Growth from Silane

The data show that SiH_4 flow rates as high as 100 cc/min are available to us without homogeneous nucleation—to a large extent independent of H_2 concentration and temperature. This will permit saturation times of 15, 30, and 75 minutes for silicon uptake experiments performed at 1000 C, 1100 C, and 1200 C respectively. These times assume 33 percent uptake efficiency and 50 percent tin coverage of the reactor area.

SILICON DEPOSITION

Several preliminary experiments have been performed in our horizontal reactor to measure the conversion of SiH_4 to silicon. These are listed in Table 1.

Table 1

RUN #	T (°C)	SiH_4 (cc/min)	HCl (cc/min)	Time (min)	Substrate	δW (g)	F
H4	1040	7.9	0	21	Sn	0.045	0.21
H6	1050	27.3	45	57	Silicon Wafer	0.623	0.32
H7	1040	10.7	0	63	Sn	0.189	0.22

The substrate for runs H4 and H7 was a pool of molten tin held in a rectangular quartz tray 3.2 cm wide by 6.4 cm long. The substrate in run H6 consisted of 2 silicon wafers presenting an area of 30 cm² to the gas stream. In addition to the SiH₄ and HCl flows shown in the table, hydrogen and nitrogen at 3.4 liter/min and 1.2 liter/min, respectively, flowed in the system in all cases.

A silicon sample was included as a substrate for several reasons: first, to act as a baseline sample to indicate whether the rate of reaction of SiH₄ at the liquid tin surface and the subsequent dissolution of the resultant silicon are grossly different than the corresponding reaction and deposition upon single crystal silicon, and second, any variation in thickness of deposit in the direction of the gas flow may be used to study the depletion of SiH₄ from the gas stream. Finally, if the total rates of deposition on the liquid and solid are comparable, the spatial distribution of silicon deposited on the solid substrate, which is easily measured, indicates the variation of silicon uptake along the liquid tin surface. This cannot be measured directly due to rf stirring of the liquid.

The substrates were weighed to an accuracy of 10 micrograms at the outset of each run. They were then inserted into the reactor and the hydrogen and nitrogen gas streams were turned on. The temperature was next brought up to the value shown in Table 1. After the temperature had stabilized, the indicated SiH₄ and HCl flows were added to the gas stream and were allowed to react with the substrates for the times shown. The active gases were then shut off, and the system cooled to room temperature. The substrates were then reweighed. The weight change was in all cases positive and is given in the column marked δW of Table 1. The SiH₄ and HCl concentration were such that homogeneous nucleation was suppressed. The ratio of the amount of silicon deposited upon the substrate (the weight gain) to the total amount of silicon that entered the reactor as SiH₄ during the run is given in the last column of Table 1.

The liquid tin dissolved approximately 20 percent of the incoming silicon in both cases; although the total silane flux varied by a factor of four. This indicates that the uptake rate of silicon by the tin is linear up to the concentration represented by the 0.189 gram of H7. The initial charge weighed 51.6 grams, yielding 30 percent of saturation.

Thirty percent of the incoming silicon is deposited upon the silicon substrate (H6) compared with 20 percent for the tin. It is, however, too early to say that this indicates a preference for deposition of silicon upon the solid, compared with the liquid. Another possible reason for the difference may be the geometry of the experiments. The tin substrate covered only 32 mm of the 57 mm width of the reactor, whereas the silicon substrates were 50 mm wide. The ratio of the two widths is 1.56, possibly accounting for the difference.

PROBLEMS

The foreign material which forms on the surface of the Sn-Si melts as "scum" constitutes a problem which must be solved. We plan to conduct experiments to identify the scum and its origin, and to find ways for eliminating it.

Section 3

TENTATIVE CONCLUSIONS AND RECOMMENDATIONS

We feel that our preliminary supercooling results are encouraging since they show that rather substantial supercooling can be achieved in the Sn-Si alloy system, even though the surface of the melt could be seen to be contaminated with a layer of foreign material. In a continuous growth apparatus, this material would be swept away during the start-up period and should not constitute a problem during subsequent operation of the furnace. Nevertheless, the values observed are within the range assumed in the analysis of surface growth presented in the technical section of our proposal.

The planar crystals that were observed growing on the supercooled Sn-Si alloy surface are similarly encouraging. They explicitly demonstrate that two-dimensional surface growth is possible at useful rates.

Finally, the initial silicon uptake experiments indicate that the incorporation rate of silicon into tin is not grossly different from the deposition of silicon upon solid substrates. This, coupled with the determination that homogeneous gas phase reactions may be suppressed by HCl, permits us to anticipate that gas phase saturation of tin melts may be accomplished in times of the order of tens of minutes.

Section 4

PROJECTED ACTIVITIES

The "scum" will be analyzed and experiments will be performed directed towards eliminating it.

We also plan to conduct another series of supercooling experiments with the melt contained in a long horizontal boat. The gas flow will be along the axis of the boat which will sweep any scum which forms toward the downstream end of the boat. This end of the boat will be maintained at a higher temperature. This arrangement will provide a closer simulation of the growth configuration anticipated for the final sheet growth furnace and should permit measurements of supercooling to be made under scum-free conditions. This form of the experiment will also provide an opportunity for the introduction of oriented seeds for more systematic studies of crystal growth at the melt surface.

Silicon uptake experiments will be performed in a systematic way covering the range 1000 C to 1200 C.

The nucleation and growth of crystalline silicon at the surface of supercooled Sn-Si melts will be investigated. Parameters to be varied are temperature, seed nature and gas ambients.

Section 5
NEW TECHNOLOGY

There are no reportable items of new technology.

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Appendix I

UPDATED PROGRAM PLAN

PROGRAM PLAN FLOATING SUBSTRATE PROCESS

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Appendix II

MAN HOURS AND COSTS

This being the first quarter of the present contract effort, there are no previous hours or costs. First quarter charges to March 28, 1976 include 532 hours of scientist/engineer effort and 576 hours of technical specialist and shop time. Total charges for this quarter are \$48,744, not including fee.

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

Floating Substrate Process

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

	This Quarter	Total To Date
Costs	\$48,744	\$48,744
Hours	1108	1108