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HEAT EXCHANGER-INGOT CASTING/SLICING PROCESS

Silicon Sheet Growth Development for the Large Area Silicon
Sheet Task of the Low Cost Silicon Solar Array Project

Second Quarterly Progress Report, January 1, 1976—March 31, 1976

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MASTER

April 6, 1976

Work Performed Under JPL Contract No. 954373

Crystal Systems, Incorporated
Salem, Massachusetts

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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by

Frederick Schmid

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SUMMARY

The object of this program is to demonstrate that large single-crystal ingots can be economically cast by the Heat Exchanger Method (HEM) and economically sliced into thin sheets with a multi-wafer slicer. Crystal Systems was funded November 20, 1975 to conduct an experimental program designed to demonstrate the potential and isolate the limiting parameters for crystal casting and slicing with the Heat Exchanger Method (HEM) and the multi-wafer slicer.

The goals for producing silicon sheet under this contract are:

Ingot Growth Project

Physical Dimensions: 6" diameter by 4" high

Growth Rate: Solidification time 8 hours

Dislocation Density: $< 10^4 \text{ cm}^{-2}$

Crystal Structure: Single crystal

Slicing Project

Physical Dimensions: 8 mils ± 1 mil thickness for sheet
cross sections of 4" diameter, 4" x 4" and 6" x 3"

Slicing Rate: 10 mils/minute (per wire/blade)

Surface Steps: 0.2 mils

Wire/Blade Thickness: 3 mils wire; 4 mils blade

Parallel Slices: 100

A vacuum resistance furnace as illustrated in Figure 1 was put into service for silicon crystal casting.

SCHEMATIC OF CRYSTAL CASTING FURNACE

Figure 1

The initial experiments were conducted to determine if silicon could be processed in vacuum.

It was demonstrated that silicon could be melted and solidified in a 0.1 Torr pressure (mechanical pump vacuum) in an open quartz crucible. The actual rate of crucible decomposition $\text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO}$ was 20,000 times slower than theory predicted. The boundary layer between the crucible and the molten silicon is not broken down due to convection; therefore, it remains highly concentrated with SiO which may chemically suppress crucible decomposition.

Processing in vacuum has a big cost advantage over processing in an inert atmosphere. In addition, it is easier to control heat flow, possible to refine the molten silicon and achieve a lower equilibrium oxygen solubility at the lower pressures.

It has been demonstrated that the silicon seed bonds to the quartz crucible bottom preventing it from floating to the surface when the silicon charge melts. For seeding the heat exchanger and furnace temperature must be determined by trial and error since the seed can not be observed. Partial seeding was accomplished on the top edge of the seed resulting in single crystal growth to the top surface of the ingot.

For crystal slicing, a multi-blade wafering technique will be used as illustrated in Figure 2. Equipment had to be developed to upgrade the current state of the art. This involved designing and fabricating a responsive feed mechanism, slurry-recovery system, and wire stretching system. The machine is now completed and capable of slicing silicon with wire.

MULTI WAFER SLICER

CRYSTAL SYSTEMS INC.

Figure 2

QUARTERLY PROGRESS

Crystal Casting

A graphite resistance furnace was prepared for casting silicon single crystals, and crystal casting was undertaken.

The initial casting goal was to optimize the refining condition, i.e., determining if silicon could be processed at 0.1 Torr, mechanical pump vacuum and determining if the crucible would have to limit the exposure of the melt to the furnace atmosphere. The initial tests showed that no severe reactions occurred for silicon melted under a 0.1 Torr pressure in an uncovered quartz crucible. The pressure was directly dependent on the temperature. At the melt temperature, the pressure was approximately 0.09 Torr (90 μ m), and it increased 1 μ m for each $^{\circ}$ C increase in temperature. This rise did not appear to be caused by evolution of gas from the chamber but from decomposition of the silica in contact with molten silicon.

Green and co-worker¹ also saw an increase in pressure when melting silicon in vacuum; they attributed this to decomposition of the crucible. The area of the crucible that was in contact with 25 $^{\circ}$ C superheated molten silicon for 30 hours was 0.5mm thinner than the area not exposed to molten

silicon. The reaction is obviously slow, possibly due to a low thermodynamic driving force or due to kinetics. No information could be found in the open literature which related the quartz decomposition by molten silicon to pressure.

It was felt that the reactions between silicon, quartz and carbon should be studied to determine the effect of pressure on crucible decomposition and oxygen solubility in molten silicon. The reactions that were considered were:

1. $\text{Si (cond)} + \text{SiO}_2 \text{ Cond} \rightarrow 2 \text{ SiO (gas)}$
2. $\text{Si (cond)} + 3 \text{ SiO}_2 \rightarrow \text{O}_2 + 4 \text{ SiO (gas)}$
3. $\text{C (cond)} + \text{CO}_2 \text{ (gas)} \rightarrow 2 \text{ CO gas}$

The conclusion reached on the basis of thermodynamic calculation is that at 0.1 Torr, the quartz crucible will decompose due to the $\text{Si} + \text{SiO}_2 \rightarrow 2 \text{ SiO (gas)}$ (1) reaction.

At 1712°K (i.e. 25°C above the melting point of silicon) the equilibrium vapor pressure is 10 Torr. The boundary condition for crucible decomposition is shown as a dotted line in Figure 1, $\log P (\text{SiO}) \text{ Torr} = 11.47 - 17900T^{-1}$.² The oxygen concentration in the silicon can be calculated for pressures below 1 atmosphere by $\log \frac{P (\text{SiO})}{N} (\text{Torr}) = 12.93 - 12870T^{-1}$. N is the atomic fraction of oxygen. The results of this equation are displayed in Figure 3 showing the phase boundaries for the formation of SiO (gas) as a function of processing temperature and concentration of oxygen in silicon.

Figure 3. EQUILIBRIUM BOUNDARY FOR THE REACTION $\underline{\text{O}}$ (DISSOLVED OXYGEN) + Si (CONDENSED) $\rightarrow$ SiO (GAS) AS A FUNCTION OF OXYGEN CONCENTRATION (IN ATOMIC FRACTION AND ATOMS/ cm^3).

Reference to Figure 1 suggests that rather low concentrations of oxygen could be attained at the low pressure end of the working range. However, at pressures below 10 Torr thermodynamics predicts that silicon reacts with the quartz crucible to form SiO. The experimental evidence to date shows that the crucible decomposition reaction $\text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO}$ is sluggish: i.e., 0.4mm/day (16 mil/day) reacted off the crucible wall. At these rates, the crucible will hold up for many days. The theoretical rate of decomposition of the crucible by Langmuir vaporization of silicon monoxide can be calculated with the following equation: $W \text{ (gms/cm}^2 \text{ sec)} = 44.4 p \text{ (atm)} M^{1/2}(\text{SiO}) T^{-1/2}$ where $M(\text{SiO})$, the molecular weight of silicon monoxide in grams is equal to 44, and T is the absolute temperature in Kelvin. The above equation yields an equilibrium rate of vaporization of 0.092 gms/cm² sec. under these conditions. The experimentally observed rate of decomposition 0.4mm/day translates to a rate of SiO evolution of 4.2×10^{-2} Sec which is 20,000 slower than the calculated equilibrium evaporation rate. This result suggests that there are rate limiting conditions which prevent copious evolution of SiO.

Stabilizing temperature gradients inherent in Heat-Exchanger Method inhibits convective flow of silicon by the crucible wall. Therefore the boundary layer is not broken down but remains highly concentrated with SiO. This would tend to chemically suppress the SiO_2 decomposition into SiO.

All the experimental evidence to date shows that it is feasible to solidify silicon in a 0.1 Torr pressure. Aside from being much less expensive than processing in an inert atmosphere, processing in a vacuum offers the following advantages:

1. It is easier to control the heat flow since there is only radiational heat transfer.
2. The equilibrium oxygen solubility in molten silicon is decreased with decrease in pressure resulting in a lower oxygen concentration: i.e., 1×10^{16} atom/cm³ at 0.1 Torr.
3. Volatile impurities can be distilled off and pumped out of the system.

On the basis of the theoretical and experimental findings, it appears desirable to continue casting silicon in a 0.1 Torr vacuum. During the seeding and growth experiments, the reaction of the crucible will be closely monitored to determine the reaction rate.

Seeding experiments were conducted in flat-bottomed crucibles loaded with 2.5 kilograms of silicon. The central area of the crucible bottoms was lapped on both sides so the 2" diameter by 0.5" thick (111) seed and the heat exchanger would make good contact.

Seeding experiments show that the seed reacts with the crucible bottom during the heatup cycle to form a bond which prevents it from floating to the surface when the silicon

charge melts. To prevent the seed from melting and to cause the crystal to grow, heat must be extracted through the quartz crucible by the heat-exchanger.

The heat-exchanger and furnace temperature for seeding must be determined by trial and error since the seed is beneath the molten silicon and cannot be observed.

The recommended thermal conductivity of quartz in the 900° to 1200°C temperature range varies from .035 to .105 watt/cm°C. This makes it difficult to make initial estimates on the heat-exchanger temperature necessary to melt into the seed without totally melting it.

During the first seeding run, a furnace failure was encountered causing a polycrystalline ingot to grow. A hemispherical growth interface was delineated apparently where the power failed. Unfortunately, no further results can be drawn from this run since the furnace failure occurred during the night, and the automatic temperature controlling and recording equipment had not yet been delivered.

The cool-down rate of this ingot was very rapid causing small interlocking crystallites to hold the ingot together.

The ingot resulting from the next run was polycrystalline since the seed totally melted out. Very large crystallites were formed due to a slow solidification rate of 1.25°C/hr. The large crystallites were not interlocking causing the ingot to break into six large pieces with many small pieces at the

crucible wall. These results are consistent with the findings for unseeded ingots. Fast cool-down rates caused small interlocking grains to hold the ingot in one piece while slow cool-down rates caused large grains that were not interlocking causing the ingot to crumble into individual crystallites.

For the next seeding experiment the heat-exchanger temperature was further lowered to assure that the seed would not melt. The molten silicon did not melt into the seed resulting in a polycrystalline ingot. The seed was totally intact and the bond to the crucible could be observed. The heat-exchange temperature was increased slightly for the next run but the liquid only melted into the top edges of the seed. This is shown in Figure 4, a photograph of a sand blasted cross-section through the seed. The outline of the seed is clearly visible. The top circumferential edge is the only area that the molten silicon melted into. Laue photographs show that this area nucleated single crystal silicon of the (111) orientation which grew conically up to the top surface of the ingot. The liquid did not melt into the top or into the lower circumference edge, hence, areas extending out from this section of the seed were found to be polycrystalline. The area directly over the seed formed columnar grains that grew to the surface. On the outer periphery of the ingot equiaxed grains formed indicating that the growth conditions were not as favorable for single crystal growth. The fact

FIGURE 4: A PHOTOGRAPH OF A SAND BLASTED CROSS-SECTION THROUGH THE SEED

that the seeded area grew completely to the top surface of the ingot is very encouraging. The growth conditions appear satisfactory for single crystal growth. The columnar grain and single crystal advanced at an angle of about 25° from the normal, this illustrates how the liquid-solid interface expands three dimensionally from the seed to the crucible wall. The resistivity of the ingot averaged about $45\Omega\text{-cm}$ in the single and polycrystalline areas.

The heat-exchanger temperature for completely melting the seed and for just melting into it have now been established. To melt into the seed sufficiently for complete seeding, the heat-exchanger temperature must be increased. This temperature range is narrowed down to less than 50°C .

CRYSTAL SLICING

The major emphasis during the first stage of the crystal slicing program was to develop a slicing machine capable of slicing silicon with wires. This involved fabricating a responsive feed mechanism, slurry-recovery system and wire stretching system. The fabrication of the new feed mechanism was completed. The original feed mechanism in a multi-blade wafer slicer was removed, and the new mechanism was installed. The new feed mechanism was necessary for slicing silicon with wires. It is capable of responding to variations in wire deflection that occur in wire slicing.

The vertical deflection of wire varies with the position of the blade carriage: it is greatest in the center and decreases as it moves toward the clamped end of the wire. To maintain a constant cutting force on the wires, the feed mechanism must be capable of responding quickly to the deflection of the wire. The blade head reciprocates at 100 cycles per minute for typical cutting; therefore, the feed mechanism must respond 200 times per minute (3.3 times/second) from the minimum to the maximum deflection. For a machine operated with wire of 0.003 inch effective diameter steel core prestressed to 100,000 PSI and with an 8-inch stroke, the wire deflection will vary from 0.3 to 0.39 inches for a feed force of 0.1 lb force/wire, (45.3 g/wire).

If the feed mechanism is too insensitive to respond to the wire deflection due to inertia and/or friction, the feed force will vary from 0.07 to 0.12 lb force/wire (31.7 to 54.3 g/wire), a variation of 41.5% in the cutting force. This is destructive to the wire since it can cause premature fatigue failure. In addition, this instability in cutting force can cause wander of the wire.

Besides being responsive to wire deflection, the new feed mechanism has the following advantages:

1. The feed force can be controlled and resolved to within .01 lb/wire (4.5 g/wire) for 25 wires or .0025 lb/wire (1.1 g/wire) for 100 wires.

2. Motion of the workpiece is incorporated in the feed mechanism so the workpiece motion can be coordinated with the motion of the blade carriage.

By control of wire tension and deflection, feed force and workpiece motion, a cut profile can be achieved which gives the desired contact between the wire and the workpiece. By generating a radial cut, high cutting pressure can be achieved with light feed force.

3. An efficient coolant/slurry recovery system is incorporated into the feed mechanism. The catch pans are designed so there will be virtually no spillage or entrapment of slurry. This allows use of expensive diamond slurries since there will be almost complete recovery. The pan system is made out of stainless steel; this will allow use of corrosive chemicals for chemical/mechanical slicing.

The wire stretching system was completed and tested. Any size and number of wires can be easily strung to a consistent tension with the wire stretching system that was developed. Wires strung with this mechanism were placed in the cutting head and stretched to failure. All the wires failed simultaneously at the predicted tensile strength. This shows that wires can be tensioned uniformly at the level of tension that is desired. A system for changing the cutting edge of blades with diamond has also been developed. It is hoped that the diamond impregnated into the wires and or blades will not dull but will remain sharp for long periods of time to cut the silicon freely.

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CONCLUSIONS AND RECOMMENDATIONS

The crystal casting tasks are on schedule. It has been demonstrated that silicon can be processed in a 0.1 Torr pressure in an open quartz crucible. The decomposition is 20,000 times less than predicted by theory. A boundary layer highly concentrated with SiO probably is chemically suppressing the crucible decomposition. For seeding it was demonstrated that the seed bonds to the quartz crucible preventing it from floating to the surface. Partial seeding was achieved on the top outer edge of the seed where the liquid melted into it. Single crystal silicon of the (111) seed orientation grew to the top surface.

For crystal slicing a responsive feed mechanism, wire-stretching system, and slurry system were completed. The machine is now capable of slicing silicon with wire.

FUTURE WORK

The emphasis in crystal casting during the next quarter will be on seeding. This will involve determining the heat exchange and furnace temperature for melting uniformly into the seed.

A total systems approach will be used to update the current multi-wafer slicing technique.

(1) The slicing machine has been made sensitive to cutting pressure.

(2) The sharpest most effective blade/wire abrasive will be used, i.e., diamond held in place on wire or blade edge.

(3) Swarth will be removed with a low viscosity fluid to prevent agglomeration and loading of the cutting tool.

(4) Chemicals such as NaOH; this will also reduce damage and prepare the surface for junction formation.

The emphasis for the next quarter will be on alternating the wire tension, cutting force, and work piece motion to achieve the optimum cutting condition.

SCHEDULE OF MILESTONES--CRYSTAL CASTING

PAGE 1 OF 2

ITEM	DESCRIPTION	Month 1976												Nov
		Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct		
1	A. Modify and calibrate	○△												
2	furnace/Purchases	●												
3														
4	B. Optimize refining		○△											
5	conditions			●▲										
6														
7	** Design & Performance		○△											
8	Review			●▲										
9	C. Establish seeding con-			○					△					
10	dition for 6" Ø x 4"			●										
11	single crystal													
12														
13	D. Establish single crystal							○				△		
14	casting parameters for													
15	pure silicon melt stock													
16														
17	E. Establish single crystal											○		
18	casting parameters for												△	
19	solar energy grade silicon													
20	melt stock													
21	F. Final Report												○△	
22														

LEGEND: ○ Estimated Start △ Estimated Complete ● Actual Start ▲ Actual Complete

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SCHEDULE OF MILESTONES--CRYSTAL SLICING

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ITEM	DESCRIPTION	Month 1976											
		Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov
1	A. Blade and equipment	○△											
2	modification and purchases	●▲											
3													
4	B. Slice silicon test piece		○			△							
5			●										
6	** Design & Performance		○△										
7	Review			●▲									
8													
9	C. Blade hardness varied and					○		△					
10	alternate blade systems												
11													
12	D. Particle size varied							○		△			
13													
14	E. Diamond type varied									○		△	
15													
16	F. Special effects on cutting											○	△
17													
18	G. Final Report												○△
19													
20													

LEGEND: ○ Estimated Start △ Estimated Complete ● Actual Start ▲ Actual Complete

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