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LARGE AREA SILICON SHEET BY EFG

Third Quarterly Progress Report, April 1, 1976--June 30, 1976

A. D. Morrison
K. V. Ravi
C. V. H. Rao
T. Surek
D. F. Bliss
L. C. Garone

June 15, 1976

Work Performed Under Contract No. NAS7-100

Mobil Tyco Solar Energy Corporation
Waltham, Massachusetts

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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Mobil Tyco Solar Energy Corporation
16 Hickory Drive
Waltham, Massachusetts 02154

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by

A. D. Morrison, K. V. Ravi, C. V. Hari Rao
T. Surek, D. F. Bliss and L. C. Garone

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ABSTRACT

The "wide" ribbon machine, JPL No. 1, is satisfactorily nearing completion. Heat sinks to accelerate growth rates were tested. Although horizontal gradients can be tailored with the heat sinks, no growth rate improvement was realized. The electrical effects of linear boundaries have been studied. Thin ribbon growth as an immediate task is reconsidered.

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INTRODUCTION

The objectives of this program are to produce at high speed, thin, wide sheets of silicon of the quality needed to fabricate 10% efficient solar cells. This is part of a total Mobil Tyco Solar Energy Corporation objective to produce silicon ribbon for solar cells at a cost which will allow their wide scale use for generation of electrical power. The edge-defined, film-fed growth process was developed for the commercial production of continuous shaped single crystals of sapphire from the melt and was applied to growth of silicon ribbon for solar cells partly under NSF Grant GI37067X via Harvard University, JPL Contract 953365, and under NSF Grant GI43873. The basic feasibility of the application of EFG to the growth of silicon ribbon has been proven and the theoretical base for extending the technique to the efficient production of single crystal silicon sheet has been established.

The two major tasks in this program to produce large area silicon sheet by EFG are: the growth of thin ribbon at high speeds in existing apparatus and the design and construction of a system for the growth of wide ribbons. These two tasks will be combined toward the end of the program to achieve the ultimate program goal. Concurrent with the development of the growth process and ribbon growth apparatus will be material and solar cell characterization programs and theoretical studies of various aspects of EFG silicon sheet growth including melt replenishment, the effect of h_{eff} and aspects of heat flow in the EFG silicon growth system.

During this third quarterly reporting period work has progressed along several fronts. The growth of ribbon at high rates is being studied both theoretically and empirically. The EFG system for wide ribbon growth will be turned on in the first days of the coming period. Details of the program follow in the Technical Discussion.

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TECHNICAL DISCUSSION

Apparatus

In the last quarterly report, ⁽¹⁾ modifications to bring a resistance heated EFG silicon ribbon furnace up to state-of-the-art specifications were described. This growth system is designated JPL No. 2. It was intended for the "thin/fast" task of this program. During this quarter, ribbon growth runs 14-167 through 14-189 were made in this system which performed satisfactorily throughout. Run results are described in the Experimental Section.

A new growth station, designated JPL No. 1, is intended for the wide ribbon task. Its turn-on milestone target is July 1. This horizontal configuration ⁽²⁾ resistance heated system will include an all stainless steel inner chamber, molybdenum and tungsten heat shields, high purity graphite heating element and crucible holder, and trough-shaped quartz crucibles.

The 6 foot fixed stroke puller will be ball screw driven by a closed-loop controlled torque-motor. The SCR controlled main power supply (25 kW, 3 ϕ) is supplemented by other (~ 10 kW total) power supplies for independently controlled die heater/trimmers and an active afterheater. The design details are nearly completed, major components have either arrived or are due imminently (Table I). Though simple and dependable, the resulting system will still be flexible enough to accommodate a host of experimental variables including 1 in. to 3 in. wide ribbon growth at speeds up to 3 in./min. The contract specified Design Review of JPL No. 1 was held during this quarter. The plans were found to be satisfactory. The specified Copy of Design and Standard Operating Procedure documents are being prepared and will be delivered on schedule.

The goal of the effort on station JPL No. 2 is the growth of 1 in. wide ribbon at rates up to 3 in./min. As the growth rate increased, various anticipated ⁽³⁾ problems with respect to excessive residual stress were observed. ⁽¹⁾ Because the growth

Table I. JPL No. 1 Revised Procurement Schedule (6/8/76)

Item	Cost Anticipated/ Expenditure	Date Ordered	Date Promised	Date Received	Service Requirement
Power supply 25 kW 3 ϕ , 208, 220, 440 V	2500/2500	1/12	6 Wks 2/23	✓	Recirculated water, 25 kW, wiring.
Puller frame weldment	1400/1500	3/8	6/25		Rigging and assembly.
Puller slide	4800/5500	3/8	5/17	✓	Rigging and assembly.
Puller motor, controller, power supply	1150/1160	Wk of 3/8	5/17	✓	Wiring, circuit design.
Furnace chamber	3500/4200	4/19	6/18		Recirculating water.
Vacuum pump	700/700	3/26	4/5	✓	110 V
Shield pack Mo/Mo-W	1000/1030		7/1		
Top heater power supply	800/1030		-	✓	Wiring, circuit design.
Graphite parts (crucible holder, heating elements, etc.)	300/~ 1000		7/1	Partial	Design, Machine Shop.
Controllers	2 at 400/ 2 at 400	-	-	✓	Wiring, circuit design.
W & Mo materials	600/1425		7/1	✓	Engineering, Machine Shop.
Cartridge parts (2 in.)	1100/?		7/1		-

rate is limited by the rate of heat removal from the interface region⁽⁴⁾ and because stress in the ribbon appears to be dependent upon the thermal gradients in the cool down region,⁽³⁾ a variety of thermal modifiers or shields for the region above the die top have been considered. Some have been tested. Figure 1 is a schematic of an assembly used. The assembly consists of two graphite blocks or "shoes" which are press fitted and pinned to water cooled stainless steel blocks. Figure 2 is an engineering drawing of the "shoes". Note that shoes with different A dimensions were designed. The shoes were subsequently modified to the configuration shown in Fig. 3. Just as the original designs preferentially cool the faces of the ribbons, these slotted shoes preferentially cool the ribbon ends. The mix was intended to show the influence and importance of horizontal thermal gradients above the hot zone. Toward the end of the quarter, some initial experiments to modify the vertical thermal gradients from temperatures around 1200°C and below were attempted. The intent was to reduce the rate of cool down of the ribbon and to achieve a linear temperature gradient in order to minimize the residual stresses in the crystals. To do this, a grafoil lined fiberform chamber was constructed and installed above the die. The results of the experiments are discussed below.

Experimental

Various profiling techniques were tried on JPL No. 2 to learn how to obtain meaningful data with respect to the objective of designing a thermal gradient which would yield low stress ribbons at high growth rates. Profiles were made on one system with a top fiberform insulating block (No. 14-166) and in another (No. 14-173) in which molybdenum shielding was used. The profiles were taken using a bare thermocouple raised at constant speed vertically from positions at the top left edge, center and right edge of the die. Profiles were also taken with a thermocouple attached to the seed (positioned by etching a slight depression in the seed) while a ribbon was being grown and while it was then being melted back to the original seed interface. The results are shown in Fig. 4 for run No. 14-166. Four centimeters of ribbon were grown at increasing pull speeds (as would occur in actual growth) to a final speed of about 1.5 in./min. The melt-back rate was 0.23 cm/min. It was apparent from these results that both the speed of profiling and the attachment of the thermocouple to the seed as well as the effects of growth were variables to be considered.

Fig. 1. H₂O cooled heat sinks in place above the die

Fig. 2. Cooled graphite block (note 3 values of dimension A).

Fig. 3. Notched cold shoes.

Fig. 4. Thermal profiles made during Run No. 14-166 (a). Free thermocouple, (b) thermocouple attached to seed during ribbon melt-back, (c) thermocouple attached to seed during growth.

In run No. 14-173 the conditions of growth were simulated and a profile obtained with the thermocouple attached to the seed as described above. The speed from the onset of seeding to stable growth is variable. Therefore profiles were then taken with an unattached thermocouple at the slowest speed (0.25 cm/min) and at the fastest speed (1.5 in./min). The resulting curves (Fig. 5) also show that the furnace gradient is best profiled with a slow moving thermocouple. In Run 14-175, a system similar to that of Run 14-173, profiles were taken with the thermocouple attached to the seed first without growth and then while growing (Fig. 6). Although the growth was very poor, the salient features of the differences in the profiling mode are clearly seen. In the initial period of growth, under continuously increasing speed, the ribbon at the thermocouple on the growing ribbon senses a steeper thermal gradient than the thermocouple which was merely suspended above the die.

During this reporting period, 24 growth runs were made. The run details and results are summarized in Tables II and IIA and III and IIIA. Most of these runs were efforts to relate growth speed or thermal geometry to ribbon stress.

In an effort to establish frowning (e.g., high in the center and lower at the ends) isotherms in the plastic region of the growing ribbon for reduced stress,⁽³⁾ frowning dies were run. These runs never achieved growth rates greater than 1.6 in./min. The ends of the die, although closer to the heat source were poorly coupled to the hot liquid reservoir and, as a result, were always very "cold". Residual stress in ribbon No. 14-170-4 from a reverse curve die measured by the splitting technique⁽⁵⁾ was 24, 642 psi. Ribbon No. 14-169-2, from a flat die in an otherwise comparable system had a measured residual stress of 24, 600 psi.

Growth runs No. 14-173, 14-174, and 14-175 were made with effective shielding between the heat source below and the growth region. In one case a trough shaped Mo shield was used to separate the zones. Wide-open fiberform shielding kept the melt hot and let the ribbon radiate freely. Growth rates up to 2.1 in./min were achieved, but the ribbon was severely stressed. Attempts to anneal these stressed and buckled ribbons were unsuccessful. The ribbons shattered every time on being loaded into the boat or furnace.

Ribbon growth run No. 14-176 was a preliminary evaluation of a new die modification, the use of end plugs of various designs. These are intended to effect a higher meniscus for thinner ribbons and provide better edge stability (Appendix). Plugs flush with the die top or with various profiles above the die top have been considered. The geometry used for this run was a flat die top profile with tips elevated

Fig. 5. Growth Run No. 14-173 temperature profiles (a) thermocouple moving at 0.25 cm/min (b) thermocouple moving at 3.8 cm/min (c) thermocouple mounted on seed-speed constantly changing.

Fig. 6. Thermal profiles (a) and (c) with thermocouples attached to the seed, but no ribbon growing and (b) and (d) during a growth run.

Table II. Growth Runs

Run No.	Date	Purpose	Die	Insulation	Comments
4-167	3/15/76	Fast growth from a two-piece die	C-10166-6	Fiberform and baffle	Thermal profile plotted.
4-168	3/16/76	Fast growth from a reverse curve die	C-10047-4	Fiberform and flat shield	Front and rear view of interface achieved for future possible automation.
14-169	3/19/76	Fast growth experiment with flat die to measure stress	C-10166-6	Fiberform opened up for fast growth. Baffle shield.	26,600 psi residual stress measured.
14-170	3/24/76	Fast growth experiment with reverse curve die. To measure stress.	C-10047-4	Fiberform opened up for fast growth. Flat shield.	24,600 psi residual stress measured.
14-173	4/2/76	Fast growth.	C-10166-6	Cold environment and Baffle shield and V-shaped shield.	Thermal profile made.
14-174	4/6/76	Fast growth.	C-10166-6	Same as above but last two ribbons grown without V-shield.	Ribbon broke when placed in quartz boat for annealing in diffusion furnace.
14-175	4/8-9/76	Fast growth from a one-piece die.	C-10436-2	Cold environment and Baffle shield.	Thermal profile made. Seed profile attempted.
14-176	4/13/76	Fast growth from a one-piece die with end plugs.	C-10436-2	Cold environment and Baffle shield.	Good possibilities if the end plugs are shaped differently.

Table IIA. Growth Run Results

Ribbon No.	Seed	Length (in.)	Avg. Width (in.)	Thickness (mils)	Max. Growth Rate (in./min)	Comments
4-167-1	(111) [110]	12	< 1	13	-	Thicker in center than at edges.
-2	(111) [110]	18	< 1	13	1.8	
-3	(111) [110]	9	< 1	13	1.5	
-4	(111) [110]	9	< 1	13	1.5	
-5	(111) [110]	25	1.0	13-12	2.0	
4-168-1	(111) [110]	17	< 1	14	1.3	Meniscus high in the center.
-2	(111) [110]	16	< 1	14	1.3	
-3	(111) [110]	11	< 1	14	1.4	
-4	(111) [110]	16	< 1	14	1.3	
-5	(111) [110]	19	< 1	14	1.6	
4-169-1	(111) [211]	13	1	12	1.5	Standard splitting technique used: 24,600 psi
-2	(111) [211]	12		13	1.6	
-3	(111) [211]	10		12	2.0	
-4	(111) [211]	24		12	2.0	
-5	(111) [211]	3		17	0.5	
4-170-1	(111) [211]	4	0.5	14	1.4	24,600 psi Faster growth not possible with this shield.
-2	(111) [211]	24	0.5	10	1.3	
-3	(111) [211]	20	0.5	10	1.2	
-4	(111) [211]	16	0.8	10	1.4	
14-173-1	(111) [110]	20	1	13	2	Severe buckling beginning at 1.8 in./min.
-2	(111) [110]	25	1	13	2.1	
-3	(111) [110]	26	1	13	2.1	
-4	(111) [110]	20	1	13	1.8	
14-174-1	(111) [110]	4	0.5	14	-	Severe buckling (~2 cm/buckle).
-2	(111) [110]	25	0.8	14	2.0	
-3	(111) [110]	24	0.9	14	0.78	
-4	(111) [110]	20	1	14	1.9	
-5	(111) [110]	25	1	14	1.78	
14-175-1	(111) [110]	10	0.75	17	< 2	Ribbons are thinner at fast speeds.
-2	(111) [110]	6	0.4	17	< 2	
-3	(111) [110]	24	1	17	< 2	
-4	(111) [110]	29	1	15	2.0	
-5	(111) [110]	14	1	15	2.0	
-6	(111) [110]	12	0.5	17	Varied	
14-176-1	(111) [211]	3	0.25	16	1.5	Spreading onto the tip causes a freeze.
-2	(111) [211]	3	0.25	16	1.5	
-3	(111) [211]	0	-	-	-	
-4	(111) [211]	0	-	-	-	
-5	(111) [211]	22	0.7	15	1.5	

Table III. Results of Growth Runs Using Heat Sinks

Ribbon No.	Heat Sinks Height (mils)	Highest Growth Rate Achieved	Ribbon Length (in.)	Comments
14-178-1	0.040	2.3	4	Exploded exiting the furnace.
-2	0.040	1.8	2	Exploded during growth.
-3	0.090	1.8	2	Exploded during growth.
14-179-1	0.100	1.6	2	Exploded during growth.
-2	0.100	2.0	8	Exploded exiting the furnace.
-3	0.180	1.6	2	Exploded during growth.
14-180				The blocks were profiled using the optical pyrometer - reflections voided the readings.
14-181-1	0.100	1.4	0.5	Exploded during growth.
-2	0.100	1.4	0.5	Exploded during growth.
-3	0.150	1.9	-	Exploded during growth.
14-182-1	0.400	-	0.5	Exploded during growth.
-2	0.200	-	8	Froze to die.
14-183-1	0.150		0.5	Exploded during growth.
-2	0.200	-	0.5	Ribbon buckled and broke.
-3	0.50		0.5	Ribbon buckled and broke.
-4	0.50	-	-	No growth, frowning isotherm.
14-185-1	0.050	-	0.5	Exploded during growth.
14-185-1	0.150	-	1	< full width.
-2	0.150	-	12	< full width.
14-186-1	-	-	-	Heating element broke.
14-187-1	0.075	1.5	8	At heights = 0.075, the blocks carry away ~450 W, froze.
-2	0.075	1.5	4	Exploded during growth.
-3	0.150	1.4	0.5	Exploded during growth.
-4	0.400	-	0.5	

Table IIIA. Results of Growth Runs Using Insulator Blocks

Ribbon No.	Insulator Block Height (mils)	Highest Growth Rate Achieved	Ribbon Length (in.)	Comments
14-188-1	300	1.8	-	Die cold.
-2	600	1.8	12	Top power up.
-3	600	1.5	4	Die lowered.
-4	900	1.5	22	Die low.
-5	150	No growth, die kept freezing.		
-6	400		1	Die froze, die low.
-7	400	1.2	12	Die low.
-8	300	1.2	13	Raised die 10 mils.
14-189-1	500	1.85	5	Too cold.*
-2	400	1.2	26	Too cold.*
-3	400	1.1	25	Exploded.*
-4	350	1.5	11	Insulating blocks at ribbon edges prevented freezing.

*Groove patterns in the ribbon surface apparently indicate cold or super cooled conditions.

~ 10 mils. When growing, it was possible to spread from a narrow seed out to the ends. However, when the melt reached the end mesas, it froze. Variations of the plugs to overcome the problem of cold die tips are planned.

Because the growth rate is limited by the rate of heat removal from the interface region, various methods for cooling have been considered. As mentioned previously, water cooled graphite heat sinks were tested during this period (Fig. 1). The results are summarized in Table III. Most of the ribbons shattered during or immediately after growth. In these cases only shards of ribbon and the seeds were recovered.

No growth rates were achieved which had not been achieved without the heat sinks. Conversely, use of the sinks did not appear to slow the process. Ribbon growth at ~2 in./min without heat sinks, although highly stressed, only occasionally spontaneously shattered. All the ribbons grown using the first generation graphite heat sinks were grown at ~2 in./min and none of these ribbons survived the growth process. In some cases buckled ribbon with the buckled regions extending to ~160 mils on either side could have broken as a result of mechanical contact with the 50 mil gap in the cooling shoes. However, ribbon No. 4-179-2 was grown to a length of eight inches beyond the heat sink before shattering, indicating that shattering is a result of high residual stresses introduced by the drastic cooling effect of the shoes. From these experiments it has been determined that the heat sinks are greatly influencing heat loss, but increasing the residual stress rather than reducing it.

Growth run No. 14-181 was an effort to effect the end cooling by introducing helium at low flow rates into the ends of the cold shoes. However, the gas affected the entire interface region uniformly, merely exaggerating all the gradients and problems experienced with cooling shoes in argon atmosphere. All the above ribbons exploded during growth.

The ribbon growth runs No. 14-182 and 14-183 were made with notched cooling blocks (Fig. 3). The purpose for using the notched blocks was to preferentially cool the ends of the ribbons rather than the faces. All of the ribbons grown during these two runs shattered. Growth runs No. 14-184 and 14-185 were instrumented follow-ons of the preceeding heat sink runs. Notched depth was half that of the previous two runs. Run No. 14-184-3 self destructed during growth. Run No. 14-184-4 grew several inches before breaking during or after a freeze. Runs No. 185-1 and 185-2 yielded 1.5 in. and 12 in. ribbons, both less than full width. Ribbon which is less than full width is typically less stressed than 1 in. wide material grown from the same

environment. Run No. 14-187 was made also using the compromise design cooling blocks. For the first two growth attempts, the blocks were located ~ 75 mils above the die top. In this position, temperatures measured inside the front and back blocks near the bottom were 361°C and 340°C respectively, and the temperature within 375 mils of the block top was 225°C . It was ascertained that the blocks were carrying away ~ 450 watts. Two ribbons were grown at 1.5 in./min. Ribbon No. 14-187-1 was 8 in. long, 18 mils thick, nearly full width. It froze to the die rather than grow faster. Ribbon No. 14-187-2 was ~ 4 in. long and growing when it exploded. The blocks were raised to 150 mils height. One half inch of ribbon grew at up to 1.4 in./min before exploding. The same situation occurred at 400 mils height. End cooling of the dies by the heat sinks was a problem to the operator throughout the series of experiments.

Run No. 14-188 was made with insulating blocks above the die. The purpose of the blocks was to passively limit the cool-down rate of the ribbon from 1200°C . Fiberform blocks lined with grafoil were used. Eight starts were made with the blocks at 140 to 900 mils above the die top. Growth rates of 1.2 to 1.8 in./min and ribbon lengths from 1 in. to 22 in. were obtained. The results were too inconsistent to indicate the better arrangement (Table IIIA). Run No. 14-189 used the same insulating blocks and better insulation about the die. The increased insulation was used in an effort to let the ribbon cool faster before it entered the blocks and at the same time to keep the die top as hot as possible. The results are shown in Table IIIA.

Characterization

Electrical Properties

The typical defect structure associated with ribbons which have resulted from sustained growth is composed of linear boundaries parallel to the ribbon edges. This structure, identified as the equilibrium defect structure, was discussed in detail in the Second Quarterly Report. In general, it was established that an equilibrium defect structure develops in ribbons following long time growth and the orientation of such crystals is $\{110\} \langle 211 \rangle$. It was also established that seed orientation has no influence on the eventual attainment of this structure but a $\{110\} \langle 211 \rangle$ seed or a ribbon seed exhibiting the equilibrium defect structure results in the immediate establishment of the equilibrium defect structure at the seed-crystal interface.

It is of interest to determine the electrical effects associated with the linear boundaries comprising the equilibrium structure. In order to do so, the scanning

electron microscope operated in the electron beam induced current (EBIC) mode has been used⁽⁶⁾. This technique permits the non-destructive imaging of electrically active defects in a semiconductor. To investigate as grown ribbons, Schottky barriers were fabricated by depositing $\sim 600^\circ\text{A}$ of Al on the ribbon surfaces after the formation of sintered Al back ohmic contacts. The investigation of diffused junctions was achieved by observing fabricated solar cells in the EBIC mode.

Figure 7 (a) shows an EBIC image of a section of a ribbon solar cell. The horizontal feature at the top of the micrograph is a portion of the top grid electrode. No external bias was applied to the device during observation. One linear boundary is observed as a dark band. The dark contrast associated with this boundary indicates that a local reduction in the beam induced current occurs when the beam crosses the defect. Figure 7 (b) is a secondary electron image of the same region as in (a) after the sample was subjected to a preferential etch. A number of linear boundaries are observable. The arrows indicate the one electrically active boundary in the region containing about 20 to 30 boundaries intersecting the surface. Examination of a number of specimens has shown that the density of electrically active boundaries is significantly less than the total boundary density in any given sample. Such an effect has previously been reported for the case of crystallographic defects in conventional Czochralski grown crystals.

Having established the fact that the electrically active defect density is lower than the total defect density, it is of interest to determine the factors that cause certain defects to be electrically active. An initial indication of the possible differences between electrically active and inactive boundaries is presented in Figs. 7 (b) and (c). The electrically active boundary shown in Fig. 7 (a) is identifiable as a low angle grain boundary in Figs. (b) and (c). The active region is seen to be composed of linear boundaries which are presumed to be twins and dislocations arrayed in rows parallel to the twin boundaries. The pits associated with the dislocations are observed in Figs. 7 (b) and (c). The other linear boundaries which have no dislocations associated with them are essentially electrically inactive under these conditions.

Figure 8 (a) is a secondary electron image of an as-grown ribbon surface which does not exhibit the equilibrium defect structure. A number of twin boundaries are evident, two of which have been identified by the arrows; A is just barely observable and B displays strong contrast in the secondary electron mode. Figure 8 (b) is a Schottky barrier EBIC image of the same region as in A. The electrically active structure is distinctly different from that observable in the secondary electron image.

Fig. 7. (a) EBIC image of linear boundaries, (b) secondary electron image of preferentially etched surface of the region shown in (a), (c) high magnification secondary electron image of the electrically active defect shown in (a) and (b)

Fig. 8. (a) secondary electron image of a region of a ribbon not exhibiting the equilibrium defect structure, (b) EBIC image of the same region as in (a), (c) and (d) show interference contrast optical micrographs of the same region at two different magnifications

The boundary A is found to be a strong recombination region displaying the typical 'dark-white' contrast associated with recombination centers⁽⁷⁾. The twin boundary at B which is very prominently displayed in the secondary electron display shows very slight recombination contrast as compared to boundary A. In addition, a curved feature at X appears in the EBIC image and is not observable at the surface in the secondary electron display. Most of the other prominent boundaries in Fig. 8 (a) are not electrically active.

Further analysis was carried out to distinguish structural or morphological differences, if any, between the electrically active boundaries A and X and the relatively inactive boundaries such as B. Figure 8 (c) is an interference contrast optical micrograph of the preferentially etched surface of the region shown in Fig. 8 (a) and (b) with the boundaries A, B and X identified. A readily apparent distinction between A and X on the one hand and B on the other is that boundaries A and X have a relatively high density of dislocations associated with them whereas boundary B is a twin boundary with very few dislocations associated with it. The curved boundary at X, shown at a higher magnification in Fig. 8 (d), is observable to be a low angle grain boundary composed of closely spaced dislocations.

From the preliminary analysis the following conclusions have been drawn regarding the electrical effects of the defect structure in EFG ribbons.

1. Typical ribbons exhibit the "equilibrium defect structure" composed of parallel boundaries parallel to the ribbon edges. Among these boundaries, only a small percentage ($\sim 5\%$) are observed to be electrically active in terms of functioning as regions of strong recombination.

2. Twin boundaries not associated with dislocations are observed to be electrically inactive as no recombination effects are observed around them. These form $\sim 90\%$ to 95% of the total defect structure.

2. The electrically active boundaries are associated with the presence of dislocations. Both high order twin boundaries with arrays of dislocations associated with them and low angle grain boundaries have been observed to be electrically active. Among these the low angle grain boundaries form the smaller percentage.

Thin Ribbon Growth

One of the goals of this program is the growth of ribbons of thickness down to 4 mils. The impetus for establishing such a goal is based upon the dual require-

ments of low material usage (low cost) and sufficient thickness of the silicon for adequate solar cell conversion efficiencies. It is the intention here to more closely examine this goal in the light of the many known variables that influence ribbon growth, the reliability of crystal growth machine components, solar cell conversion efficiencies and the possible impact on yield and cost. An examination of these variables indicates that very thin ribbon growth is probably undesirable and the possible economic advantages of thin ribbons are significantly offset by other factors. To analyze this proposition succinctly, the various parameters that are affected by thin ribbons will be discussed separately.

Growth Related Factors

A detailed discussion of the factors that influence shape stability in EFG ribbon growth is presented in the Appendix and References therein. A summary of the salient points relating to thin ribbon growth will be presented here.

Ribbon thickness t can be expressed as follows:

$$t = (t_d, s, h_{\text{eff}}, \phi_o)$$

where t_d is the thickness of the die top, s is the meniscus height, h_{eff} is the effective height of the growth interface above the liquid level in the crucible and ϕ_o is the angle between the tangent to the meniscus and the growth axis. Among these parameters, ϕ_o is a material parameter being related to factors such as the local orientation of the crystal surface. The other parameters, t_d , s and h_{eff} that control ribbon thickness are process or equipment related variables. Consequently, the sensitivity of ribbon thickness to these variables is of concern.

Shape stability in growth can be associated with the magnitude of dt/ds . Low $|dt/ds|$ will result in greater stability. From Figs. 2 (a) to (c) in the Appendix, it follows that t , the ribbon thickness, is more stable as s and h_{eff} decrease.

A more explicit dependence of the uncertainty in t due to uncertainties in the other geometric or process related variables results from the equation:

$$\Delta t = \left| \frac{\partial t}{\partial t_d} \right| \Delta t_d + \left| \frac{\partial t}{\partial s} \right| \Delta s + \left| \frac{\partial t}{\partial h_{\text{eff}}} \right| \Delta h_{\text{eff}} + \left| \frac{\partial t}{\partial \phi_o} \right| \Delta \phi_o$$

An examination of small changes in each of the variables t_d , s and h_{eff} and influence of these changes on changes in ribbon thickness Δt should indicate the sensitivity of the process.

Tables IV.: The Sensitivity of Ribbon Thickness to Changes in the Geometrical Variables. See Text for Discussion.

$t_d = 0.012 \text{ in.}$	$h_{\text{eff}} = 0.75 \text{ in.}$	
$t \text{ (in.)}$	0.004	0.008
$s \text{ (in.)}$	0.0128	0.0076
$ \partial t / \partial s $	0.85	0.66
$ \partial t / \partial h_{\text{eff}} $	0.0046	0.0018
$ \partial t / \partial \phi_o \text{ (in./deg)}$	0.00052	0.00030
$\Delta t \text{ (in.)}$	± 0.0035	± 0.0027

Table V. The Sensitivity of Ribbon Thickness to Changes in the Geometrical Variables. See Text for Discussion

$t_d = 0.012 \text{ in.}$	$h_{\text{eff}} = 1.50 \text{ in.}$	
$t \text{ (in.)}$	0.004	0.008
$s \text{ (in.)}$	0.0102	0.0064
$ \partial t / \partial s $	1.16	0.85
$ \partial t / \partial h_{\text{eff}} $	0.0030	0.0010
$ \partial t / \partial \phi_o \text{ (in./deg)}$	0.00042	0.00024
$\Delta t \text{ (in.)}$	± 0.0039	± 0.0030

Table VI. The Sensitivity of Ribbon Thickness to Changes in the Geometrical Variables. See Text for Discussion.

	$t_d = 0.016 \text{ in.}$		$h_{\text{eff}} = 0.75 \text{ in.}$
$t \text{ (in.)}$	0.004	0.008	0.012
$s \text{ (in.)}$	0.0169	0.0128	0.0076
$ \partial\tau/\partial s $	1.01	0.85	0.66
$ \partial\tau/\partial h_{\text{eff}} $	0.0084	0.0046	0.0018
$ \partial\tau/\partial\phi_o $	0.00070	0.00052	0.00030
$\Delta t \text{ (in.)}$	± 0.0041	± 0.0035	± 0.0027

Table VII. The Sensitivity of Ribbon Thickness to Changes in the Geometrical Variables. See Text for Discussion.

	$t_d = 0.016 \text{ in.}$		$h_{\text{eff}} = 1.50 \text{ in.}$
$t \text{ (in.)}$	0.004	0.008	0.012
$s \text{ (in.)}$	0.0130	0.0102	0.0064
$ \partial\tau/\partial s $	1.42	1.16	0.85
$ \partial\tau/\partial h_{\text{eff}} $	0.0060	0.0030	0.0010
$ \partial\tau/\partial\phi_o $	0.00062	0.00042	0.00024
$\Delta t \text{ (in.)}$	± 0.0048	± 0.0039	± 0.0030

Δt_d , the change in die top dimension can arise as a result of machining tolerances, which would be more critical as t_d decreases for thinner ribbon growth. In addition, small distortions of the die top due either to thermal effects or due to the formation of SiC particles on the die top would also adversely affect thickness control of thin ribbons. In general, $\left| \partial t / \partial t_d \right| \approx 1$ independent of other variables. Consequently, any changes in t_d are immediately reflected in changes in t . Die top dimensional tolerances are not expected to be better than ± 0.001 in.

The change, Δs , in the meniscus height is associated with temperature fluctuations both on a short term and long term basis. In addition, s is also a function of h_{eff} . Present range of control in Δs is ± 0.002 in. with long time prospects of ± 0.001 in.

h_{eff} changes continuously as the melt level in the crucible drops. With melt replenishment, it should be possible to keep Δh_{eff} to within 0.050 in.

ϕ_o changes by about $\pm 1^\circ$ and is largely related to local crystal orientation effects.

Tables IV to VII illustrate the greater sensitivity of thin ribbons to changes in the various geometrical variables. Tables IV and V show t and s values and the values of $\left| \partial t / \partial s \right|$, $\left| \partial t / \partial h_{\text{eff}} \right|$ and $\left| \partial t / \partial \phi_o \right|$ for 4 mil and 8 mil thick ribbons grown from 12 mil dies ($t_d = 12$ mils) and Tables VI and VII show the same values for 4, 8 and 12 mil ribbons grown from dies with $t_d = 16$ mils. In both cases, the data has been computed for two values of h_{eff} . Δt values have been calculated using the following values: $\Delta t_d = \pm 0.001$ in., $\Delta s = \pm 0.002$ in., $\Delta h_{\text{eff}} = \pm 0.050$ in. and $\Delta \phi_o = \pm 1^\circ$.

Some of the conclusions to be drawn from these tables are as follows: The main contribution to Δt comes from the $\left| \partial t / \partial s \right| \Delta s$ term, with the next most important contribution coming from the $\left| \partial t / \partial t_d \right| \Delta t_d$ term, which is $\approx \Delta t_d$. As s increases (for given t_d and h_{eff}) and thus causes a decrease in t , the error Δt not only increases due to the Δs term but also due to the other terms. Increasing h_{eff} also increases the Δs contribution to Δt , offsetting the decrease that occurs due to the other variables.

Δt is observed to be larger for thinner ribbons under all conditions shown in the table attesting to the greater sensitivity of thin ribbons to growth variables.

Influence of Ribbon Thickness on Cell Efficiency

Under ideal circumstances, the efficiency or the output of a silicon solar cell decreases with decreasing thickness below about 20 mils (500 μm).⁽⁸⁾ However, factors such as the bulk diffusion length and surface recombination losses have a

strong influence on the thickness dependence of cell output. Thin solar cells (e.g., 4 mils (100 μm)) would only become undesirable if the quality of the bulk silicon is such that minority carrier diffusion lengths of the order of the cell thickness can be realized and the added cost or difficulty of incorporating a back surface field⁽⁹⁾ to reduce back surface recombination effects becomes undesirable. Consequently, the desirability of growing ribbons down to thicknesses of 4 mil (100 μm) would be dependent upon the quality improvements that are made as well as on the cost factors associated with cell processing technology. If the bulk diffusion lengths cannot be increased to the 100 μm or greater levels, thin ribbon solar cells should not suffer undue efficiency losses. However, present expectations are that minority carrier diffusion lengths in excess of 100 μm will be realized in EFG ribbons. Current diffusion length values range from 30 to 80 μm . Consequently, the economics associated with thin cells would have to incorporate the added costs, if any, associated with the formation of a back junction to reduce the surface recombination velocity.

Cost Factors

The primary impetus for reducing ribbon thickness is, of course, the economic factor. Reduced silicon usage would reduce the final cost of the system. Among the three productivity parameters; ribbon width, ribbon growth rate and ribbon thickness, thickness appears to have the least impact on cost. One economic model⁽¹⁰⁾ has demonstrated that the cost of ribbon per unit area is least influenced by ribbon thickness but is strongly influenced by growth rate and width.

To summarize the current thinking on thin ribbon growth, three interrelated factors have to be considered. These are: (a) ribbon growth variables (b) solar cell efficiencies and (c) cost factors. As discussed above, with decreasing ribbon thickness, the technological problems of growth become more formidable. Component tolerances and accuracy of process control are more critical for thin ribbon growth.

Although desired cell efficiencies should be realizable, the cost factors associated with sophisticated cell fabrication techniques will partly offset the decreased cost of thin ribbons.

Finally, economic consideration should take cognizance of the potential availability of low-cost poly silicon in the future. With reduced poly costs, thinner ribbons may not be needed, thus allowing a greater degree of flexibility in ribbon growth, low-cost device process technologies, handling techniques that are less

sophisticated than would be needed to handle thin ribbons and increased product yield as a result of a less sensitive process technology.

Problems

No problems in meeting program goals have been encountered. All elements of the program are on schedule.

Plans

During the coming period JPL No. 1 will be turned on, and 2" wide ribbons will be grown. Afterheater/heat sinks will be designed and built for JPL No. 2 for minimizing stress in ribbons grown at high speeds ($> 1"/\text{minute}$). Emphasis on the thin ribbon task will be reduced.

REFERENCES

1. A. D. Morrison, K. V. Ravi, C. V. Hari Rao, T. Surek, D. F. Bliss, and L. C. Garone, "Large Area Silicon Sheet by EFG", Second Quarterly Progress Report, ERDA/JPL 954355/76-1 (1976).
2. Proc. First Task Integration Session, LSSA Project, JPL Doc. No. 5101-2, ERDA/JPL-1012-76-1 (Jan. 1976).
3. T. Surek, to be published.
4. H. E. LaBelle, Jr., A. I. Mlavsky, and B. Chalmers, "Growth of Controlled Profile Crystals from the Melt, Parts I-III, Mat. Res. Bull., 6 (1971).
5. H. E. LaBelle, Jr., G. F. Hurley, and A. I. Mlavsky, "Continuous Single Crystal Sapphire Filaments and Ribbon," Technical Report AFML-TR-66-246, Part III, June 1969.
6. J. J. Lander, H. Schreiber, and T. M. Buck, Appl. Phys. Lett., 3, 206 (1963).
7. K. V. Ravi, C. J. Varker and C. E. Volk, J. Electrochem. Soc. 120, 534 (1973).
8. H. J. Hovel, Semiconductors and Semimetals, Vol. 11, Solar Cells, Academic Press (1975).
9. J. Mandelkorn, and J. H. Lamneck, Jr. Proc. 9th IEEE Photo. Spec. Conf. p. 66, IEEE New York (1972).
10. G. H. Schwuttke, T. F. Ciszek, and A. Kran, "Silicon Ribbon Growth by a Capillary Action Shaping Technique," Third Quarterly Progress Report, ERDA/JPL 954144 (1976).

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APPENDICES

1. An Updated Program Plan

Table VIII, no changes.

2. Man Hours and Costs

Previous man hours were 2481 and cost plus fixed fee was \$79,518. Man hours for April plus May were 864 and cost plus fee was \$41,025. Man hours and cost for June are estimated to be 499 and \$17,678 respectively. Therefore, third quarter man hours are estimated to be 1363 and cost plus fee to be \$58,703. Cumulative three quarter man hours and costs plus fixed fee are estimated to be 3844 and \$138,221 respectively.

3. Engineering Drawings and Sketches Generated during the Reporting Period

Figures 2 and 3.

4. Summary of Characterization Data Generated during the Reporting Period

Using EBIC analysis it has been determined that only ~5 to 10% of the total density of linear defects are electrically active. The electrically active boundaries have been determined to be associated with dislocations. Twin boundaries not associated with dislocations are electrically inactive and these comprise ~80 to 90% of the total defect density.

5. Action Items Required by JPL

None

6. New Technology

No reportable items of new technology.

There is no cumulative new technology.

7. Deliveries

Materials specified have been delivered to JPL.

8. Stability Paper

Table VIII. Updated Program Plan

*Financial and Technical Reports Solar Cells and Samples will be delivered as per the Delivery Schedule of this contract.

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APPENDIX 8

STABILITY PAPER

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SURFACE MORPHOLOGY AND SHAPE STABILITY IN SILICON RIBBONS
GROWN BY THE EDGE-DEFINED, FILM-FED GROWTH PROCESS

by

T. Surek, C. V. Hari Rao, J. C. Swartz and L. C. Garone
Mobil Tyco Solar Energy Corporation
16 Hickory Drive
Waltham, Massachusetts 02154

ABSTRACT

The morphology and shape stability of silicon ribbons grown by the edge-defined, film-fed growth (EFG) technique is described. A theoretical analysis of shape stability is presented for controlled-shape growth (where the ribbon shape is determined by the shape of the meniscus); experimental evidence is introduced to show the inherent stability of the ribbon side and the relative instability of the ribbon edges, in agreement with the theory. The characteristic meniscus angle ϕ_0 for constant-dimension growth is shown to depend on the crystallographic orientation of the ribbon surface; the ϕ_0 -anisotropy is associated with the anisotropy in the crystal-vapor surface free energy in silicon. Growth features which result from faceted growth on peripheral octahedral planes are described, and the competition between faceted growth and controlled-shape growth is analyzed. Various morphological features associated with variations and fluctuations in the EFG process variables are described.

INTRODUCTION

There is considerable interest in applying the edge-defined, film-fed growth (EFG) process to the production of ribbon-shaped crystals of silicon for solar cell applications.⁽¹⁻⁴⁾ In the EFG method, a capillary die conducts the melt from the crucible to the crystal growth interface just above the top of the die (Fig. 1). The resultant shape of the crystal is determined by the shape of the liquid film (or growth meniscus) which, in turn, is controlled by the perimeter of the die top. In essence, then, crystals of any desired cross-sectional shape can be grown by this technique using an appropriately designed die top. Deviations from controlled-shape crystal growth can occur, however, as a result of the crystallization properties of the material.⁽⁵⁾

The fundamental physical problem in controlled-shape crystal growth is the geometric relationship between the meniscus and crystal surface directions at the crystallization front. Recent experiments⁽⁶⁾ have shown that the requirement for the constant cross-sectional growth of silicon crystals is that the angle ϕ between the tangent to the meniscus and the growth axis be a constant designated as ϕ_0 (for {111} orientation Si crystal surface, $\phi_0 = 11^\circ$). Complete analysis of the meniscus shape then shows that the ribbon thickness is related to the die and meniscus geometries by an expression of the form:^(3,7)

$$t = f(t_d, s, h_{\text{eff}}, \phi_0), \quad (1)$$

where t_d is the die thickness, s is the height of the meniscus or growth film and h_{eff} is the effective height of the growth interface above the liquid level in the crucible (see Fig. 1). From the known functional form of f and the experimentally measured values of the other parameters, the ribbon thickness can be readily calculated; good quantitative agreement has been found⁽⁷⁾ between the experimental and theoretical values of the ribbon thickness.

The stability of the ribbon dimensions (such as the thickness) in controlled-shape growth will be a function of the process parameters t_d , s and h_{eff} , and of the material parameter ϕ_0 . Variations in the die thickness can, of course, occur during growth as a result of mechanical changes in the edge-defining die dimensions (say, caused by chemical reaction of the die with liquid silicon). The variable s , in practice, is determined by the details of the heat balance at the crystallization front; for steady-state growth, the rate of heat removal by conduction-radiation through the ribbon must be equal to the sum of the rate of latent heat generation at the interface and the rate at which heat arrives to the interface by conduction through the meniscus film. Perturbations in the parameter h_{eff} can occur as a result of fluctuations in the melt level in the crucible or in the rate of crystal growth (if viscous flow effects in the die capillary are appreciable); in addition, h_{eff} continuously changes during growth as the melt in the crucible is depleted. The angle ϕ_0 has been shown previously⁽⁶⁾ to depend on the orientation of the crystal surface; the anisotropy of ϕ_0 undoubtedly results from the anisotropies of the crystal-vapor and crystal-liquid interfacial free energies of silicon.

In this paper, we examine the theory of ribbon shape stability in EFG as a function of perturbations in the geometrical variables, and present experimental evidence of ϕ_0 anisotropy effects on ribbon shape. We then consider the effects of the anisotropic crystallization properties (i.e., faceting) of silicon on controlled-shape growth based on observations in EFG ribbons. Finally, we examine various morphological features frequently observed in EFG silicon ribbons which are primarily associated with variations or fluctuations in the process variables during growth.

THEORY OF EFG RIBBON SHAPE STABILITY

The criterion for the stability of the external shape of a crystal in a meniscus-controlled process such as EFG derives from the finding⁽⁶⁾

that the crystal dimension changes when $\phi \neq \phi_0$; the relevant crystal dimension increases when $\phi > \phi_0$ and decreases when $\phi < \phi_0$. Shape stabilization takes place when the resultant change in crystal dimension is such that ϕ approaches ϕ_0 again. A condition of shape instability, on the other hand, occurs when ϕ deviates even further from ϕ_0 as a result of the shape change. This criterion was recently applied⁽⁸⁾ to the various techniques of crystal growth from the melt (Czochralski, floating zone and EFG of various crystal shapes); here we consider the shape stability of EFG ribbons when the growth is subjected to perturbations in the geometrical variables discussed above. The analysis is divided into separate discussions of the thickness and width dimensions of the ribbon.

Stability of the ribbon thickness

Figure 2a shows the variation of ribbon thickness with meniscus height for typical values of the experimental variables (i.e., solution of Eq. (1) for $h_{\text{eff}} = 2$ cm and $t_d = 0.04$ cm). The curve for $\phi = \phi_0 = 11^\circ$ represents all possible pairs of s - t values for growth with a uniform thickness. If a steady-state system (s_A, t_A) in Fig. 2a is perturbed by raising the meniscus height to B, the ribbon thickness should decrease (since $\phi < \phi_0$ at B) to a new steady-state thickness t_B . Similarly, a lowering of the meniscus height to C in the figure will lead to a new steady-state thickness t_C .

A perturbation in the die thickness t_d is considered in Fig. 2b. When the die thickness increases from t_{d1} to t_{d2} , the initially steady-state system (s_A, t_A) in the figure will fall on the dashed curve $\phi > \phi_0$ for the larger die thickness. It is readily seen that the ribbon thickness should therefore increase to a new steady-state value t_B . Of course, changes in meniscus height may also occur (as a result of changes in the thermal profile accompanying the t_d -change), but these can be accommodated in a stable manner (cf. Fig. 2a). Localized fluctuations in the die thickness occur frequently in silicon ribbon EFG when graphite dies are used (e.g., as a

result of the growth of SiC particles at the die top). A change in the effective die thickness from t_d to the capillary spacing t_c (see Fig. 1) can occur when a critical value of the meniscus height is exceeded; at this height, the angle between the meniscus and the horizontal at the die edge is equal to 30° (the wetting angle of liquid Si on graphite⁽⁹⁾). For the case examined in Fig. 2a, the critical height is 0.10 cm, thus it is not reached before the ribbon thickness becomes zero. Growth (with a new steady-state thickness) would continue from the inner edges of the die in Fig. 1 if this critical meniscus height were exceeded.

A fluctuation in h_{eff} is examined in Fig. 2c. Here we consider a hypothetically large change in h_{eff} from 4 cm to 2 cm; the initially steady-state system (s_A, t_A) is again seen to respond to this change by attaining a new steady-state thickness t_B . A similar stabilizing behavior is seen in Fig. 2d when the characteristic value of ϕ_o changes from ϕ_o^1 to $\phi_o^2 < \phi_o^1$ (say, as a result of a change in the orientation of the ribbon surface caused by twinning).

Stability of the ribbon width

The treatment of the stability of the width dimension of the ribbon is perforce less satisfying than that of the thickness dimension. The principal difficulty arises in attempting to calculate the meniscus shape near the end of the ribbon where the radius of curvature of the ribbon surface changes continuously from infinity along the side of the ribbon to approximately $t/2$ at the very end of the ribbon (see Fig. 1). An approximation to the ribbon-end problem was obtained⁽⁸⁾ by considering the shape stability of a rod-shaped crystal of radius $t/2$ growing from a die shaper with a wetted top surface of radius $t_d/2$. Figure 3a shows the variation of $t/2$ with meniscus height for $h_{\text{eff}} = 2$ cm and $t_d = 0.04$ cm. The solid line in the figure (where $\phi = \phi_o = 11^\circ$) again represents all possible pairs of $s - t/2$ values for steady-state growth. It can be readily argued in the figure that

a steady-state point such as A is stable whereas a point such as D is unstable when the meniscus height is perturbed from the respective steady-state values. In the latter case, for example, an increase in meniscus height to E will result in a decrease in the crystal radius $t/2$ (since $\varphi < \varphi_0$); this will lead to a still greater deviation of φ from φ_0 , and thus to an even faster decrease in radius, and so on. It is readily seen in Fig. 3a that the entire portion of the $\varphi = \varphi_0$ curve where $ds/d(t/2) > 0$ is unstable, whereas shape stabilization occurs in the region where $ds/d(t/2) < 0$. The detailed analysis⁽⁸⁾ of the ribbon end problem shows that the requirement for shape stability is that the edge-defining die radius ($t_d/2$) should not exceed approximately twice the radius of curvature of the ribbon ($t/2$) at the ribbon edge.

The conclusion we reach from the above analysis of the ribbon shape stability is that the side of the ribbon (i.e., the thickness dimension) is inherently stable, whereas the ribbon edge (and, therefore, the width dimension) is only conditionally stable. Perturbations in the geometrical variables at the ribbon edge can readily upset the condition of shape stability, as demonstrated in Fig. 3b. Here we see that an increase in the edge-defining die radius from t_{d1} to t_{d2} , has resulted in an initially stable system (s_A , $t_A/2$) to fall on a curve with $\varphi > \varphi_0$ for the new die radius; the system will be unstable with the radius increasing at an ever increasing rate. In the following sections, we present the results of experimental investigations of the ribbon shape stability, and show frequent examples of the inherent stability of the ribbon side and the comparative instability of the ribbon edge.

EFFECTS OF MENISCUS ANGLE ANISOTROPY ON SHAPE STABILITY

Previous experience⁽⁶⁾ has indicated that the characteristic value of the meniscus angle for the steady-state cross-sectional growth of silicon crystals (i.e., φ_0) is a function of the orientation of the crystal surface. This dependence is probably the result of the influence of the surface-free energies of the three interfaces on the relative directions of the interfaces at the crystal-liquid-vapor triple junction.⁽¹⁰⁾ In this section, we report

some morphological observations in EFG ribbons which confirm the existence of a ϕ_0 -anisotropy in silicon crystal growth; the observations are extended to obtain a measure of the anisotropy in the crystal-vapor surface-free energy in silicon. It should be pointed out here that the $\phi = \phi_0$ requirement is satisfied when the crystal shape is controlled by the shape of the meniscus; when faceted growth occurs on peripheral regions of the solid-liquid interface, this condition is no longer satisfied, as described in the next section.

Crystal defects which have been observed frequently in EFG silicon ribbons are twin boundaries.^(3, 4) Examples of twin boundary traces on the surface of the ribbon are shown in Fig. 4 for typical low-index seed orientations used in silicon ribbon EFG; the twins extend through the entire thickness of the ribbon. The occurrence of such twinning generally leads to a change in the crystallographic orientation of the ribbon surface and to a change in the growth direction. Since the meniscus height was kept constant in the experiments, the only plausible explanation for the readily visible change in ribbon thickness (see Fig. 4) is that the characteristic value of ϕ_0 has changed upon twinning. In effect, the twinning has resulted in a perturbation in ϕ_0 (cf. Fig. 2d); the deviation of the instantaneous meniscus angle from the "new" ϕ_0 during a brief transient period following the twinning then accounts for the change in the ribbon thickness.

Measurements of the thickness change in EFG ribbons were made using a Sloan Dektak surface profile recorder; the results are summarized in Table I. The table lists the average surface elevation change (and rms deviation) across the twin boundaries for a number of surface profile traces; the traces were made in both directions across the twin (e.g., $\{111\}$ to $\{115\}$ as well as $\{115\}$ to $\{111\}$). The elevation change is typically several microns (the change in ribbon thickness is approximately twice the elevation change), and the transient occurs over a ribbon length of a few tenths of a mm (the growth rate was 1 to 2 cm/min in the experiments and the ribbon thicknesses were in the range of 0.02 cm to 0.04 cm).

From the signs of the elevation changes in Table I, we can immediately deduce the relative values of ϕ_o for the various crystal surface orientations: viz., $\phi_o \{111\} > \phi_o \{115\}$, $\phi_o \{110\} > \phi_o \{114\}$ and $\phi_o \{100\} < \phi_o \{122\}$. From a model⁽¹⁰⁾ which balances the surface tensions at the crystal-liquid-vapor triple junction, one expects that a decrease in ϕ_o would be associated with an increase in crystal-vapor surface free energy. Indeed, the above variations in ϕ_o are consistent with the probable order of the surface-free energies for these low-index faces. A simple calculation based on the assumption that the surface energy for each plane varies in proportion to its area resolved in nearest $\{111\}$ planes gives the ratio of the surface free energies $\gamma \{111\} / \gamma \{122\} / \gamma \{110\} / \gamma \{114\} / \gamma \{115\} / \gamma \{100\}$ as 1.0/1.15/1.22/1.41/1.46/1.73. With the exception of the $\{122\}$ to $\{100\}$ transition (where only a small elevation change is observed), the magnitudes of the elevation changes are seen to reflect the change in the surface free energy. The value of ϕ_o is also expected to depend on the direction and free energy of the solid-liquid interface at the triple junction.⁽¹⁰⁾ It is seen in Table I that the crystal growth direction also changes upon twinning; in fact, the last two entries in the table show that a change in the growth direction alone can lead to a change in surface elevation (i.e., a change in ϕ_o). Unfortunately, without the knowledge of the detailed shape of the solid-liquid interface at the triple junction, it is not possible to speculate about the anisotropy in the solid-liquid surface free energy from these results.

Similar transient variations are observed in the width dimension of the ribbon when a twin or other high angle grain boundary emerges at the ribbon edge. Examples of twins initiating from and terminating at the edge of the ribbon are shown in Figs. 5a and 5b, respectively; Fig. 5c shows the change in ribbon width occurring when a high angle grain boundary intersects the surface at the ribbon edge. The changes in ribbon width are seen to be several orders of magnitude greater than the thickness changes in Table I. Of course, it is not practical to describe these variations in

ribbon width in terms of a change in crystal surface orientation (which, clearly, is a variable around the ribbon edge). The perturbation now is in the "distribution" of ϕ_0 around the edge of the ribbon which, together with the detailed kinetics of the crystal growth (such as the faceting effects described in the next section), leads to a change in ribbon width. The perturbations at the ribbon edges, as seen in the photographs in Fig. 5, are far more severe than at the ribbon sides, and can frequently lead to large-scale variations in the ribbon width and, on occasion, to an arrest in stable ribbon growth. This would be expected from the shape stability considerations described in the preceding section, where it was shown that the ribbon end stability was a sensitive function of the relative dimensions of the ribbon edge and the die edge.

Figure 6 shows an extreme case of edge instability where many high angle grain boundaries have nucleated in the vicinity of the ribbon edge; the width dimension is seen to be extremely unstable under these conditions. It is not clear at this time, however, whether the polycrystalline structure has resulted from the width being unstable and the growth conditions fluctuating, or the width instability is caused by the polycrystalline growth.

Finally, it should be pointed out that the present examples (Figs. 4 and 5) used to demonstrate the effects of ϕ_0 -anisotropy were obtained in the proximity of the seed (i.e., within about 10 cm of ribbon growth) where large single crystal areas are frequently observed. At larger distances from the seed, the seeded orientation is lost as a result of interactions of primary twins, higher order twins and various other grain boundaries. Recent evidence⁽¹¹⁾ indicates that, irrespective of the seed orientation, an equilibrium defect structure eventually develops in the ribbon; the orientation is approximately (110) $[\bar{1}12]$ and the ribbon contains a high density of linear boundaries parallel to the growth direction (an

example of this structure is shown in a later section). The effects of the ψ_0 -anisotropy are nevertheless observed in all EFG ribbons; the slight changes in surface elevation which result from the ψ_0 -anisotropy, in fact, cause the various boundaries to be readily discernible in the as-grown ribbon.

EFFECTS OF FACETING ON RIBBON SHAPE STABILITY

An important consideration in attempting to achieve controlled-shape growth involves the crystallization properties of the material. Because of the anisotropy in growth rate, silicon often exhibits singular (i.e., faceted) growth on regions of the crystallization front near the $\{111\}$ orientations. When such faceted growth occurs on peripheral regions of the solid-liquid interface, various ridge-like features result on the crystal surface; such features have been previously observed and analyzed in silicon crystals grown by the Czochralski⁽¹²⁾ and floating zone⁽¹³⁾ methods and in germanium crystals grown by the Stepanov technique.⁽⁵⁾ The basic effect of faceted growth on the external shape of the crystal is that the latter is no longer uniquely determined by the shape of the meniscus at the crystal-liquid-vapor triple junction (i.e., by the $\psi = \psi_0$ requirement), but it is also affected by the detailed kinetics of the layer nucleation and growth on the facets.

All descriptions of faceted growth in silicon consider supercooling as the basis of its origin; for a $\{111\}$ facet to appear at the solid-liquid interface and for growth to be maintained, a greater supercooling of the melt is required at the faceted region of the crystallization front in order to nucleate the new layer sources. Clearly, then, the shape of the freezing isotherm and its relationship to the close-packed $\{111\}$ planes affects the faceting tendency and the location of the facets. In general, peripheral faceting is enhanced by a concave (toward the melt) freezing isotherm near the periphery; the tendency to facet is also expected^(5, 12, 13) to increase with increasing

crystal growth rate, decreasing melt temperature or gradient in the melt at the growth interface, increasing impurity concentration in the melt, and decreasing concentration of crystal dislocations (which can serve as easy nucleation sites for new $\{111\}$ growth layers). In turn, faceting affects the distribution of dislocations and impurities in the grown crystal. The location of the ridge-like surface features is determined by the anisotropy of growth rate of ledges in various directions on the close-packed (111) surface; the "easy" growth directions (where the ridges appear) correspond to the $[\bar{1}\bar{1}2]$ directions, whereas lateral growth is much slower in the $[11\bar{2}]$ directions.⁽¹³⁾

Faceted growth has also been observed frequently, albeit unpredictably, in EFG silicon ribbon growth. The occurrence of faceting is observed during growth by a localized rise (or, on occasion, a fluctuating rise and fall) in the crystallization front; following growth, faceting is evidenced by the various characteristic growth features on the external surface of the ribbon. Below, we describe some typical features observed at the side and edge surfaces of EFG ribbons.

Faceting at the ribbon sides

The most frequently observed feature of growth faceting is illustrated in Fig. 7. During growth, a sharp, angular rise in the meniscus height is observed about a high angle grain boundary (twin boundary in Fig. 7); the tilt of the growth interface on either side of the boundary depends on the orientation of the $\{111\}$ planes relative to the growth direction. In the grown ribbon, faceting is evidenced by the breaks in the horizontal surface striae which delineate the instantaneous shape of the solid-liquid interface. (A detailed description of the surface striae is given in a later section). In the example shown in Fig. 7, the ribbon surface orientation is near (110) and the growth direction is within a few degrees of the $[\bar{1}\bar{1}2]$ orientation

(i.e., approximately $[3\bar{3}5]$) on either side of the twin boundary. Faceted growth thus occurs on the $(1\bar{1}1)$ planes, as shown in the sketch in Fig. 7; the angle of $\sim 13^\circ$ measured from the striae in the figure is close to the value of 14.4° for the angle between the $(1\bar{1}1)$ and $(3\bar{3}5)$ planes.

Growth faceting of the type depicted in Fig. 7 is not restricted to faceting only on peripheral regions of the solid-liquid interface; rather, the entire interface across the thickness of the ribbon can be faceted, as shown in the sketch. Indeed, corresponding breaks in the surface striae can be seen on the reverse side of the ribbon in Fig. 7. Nucleation of new growth layers is likely to occur in these cases along the line of intersection of the two facets where the supercooling is the greatest. For a typical vertical gradient in the liquid of $150^\circ\text{C}/\text{cm}$ in EFG ribbon growth, we estimate a maximum supercooling of $\sim 0.4^\circ\text{C}$ from Fig. 7. This undercooling is considerably less than the value of 6°C estimated from studies of faceting in float-zoned silicon crystals⁽¹³⁾; the difference is probably the result of the easy nucleation site at the intersection of the facets in this case.

Examples of another type of peripheral faceting are shown in Fig. 8. When the ribbon surface is very close to a $\{111\}$ orientation, we frequently obtain surface segments which are extremely smooth or mirror-like. The presence of such "surface facets" is evidenced by a lack of continuity of the horizontal surface striae across these regions, as indicated by the arrows in the figures. Basically, the crystal here exhibits a tendency to extend the low energy $\{111\}$ external surface, irrespective of the shape which is commanded by the instantaneous meniscus shape (and the $\varphi = \varphi_0$ requirement). When the ribbon surface plane is slightly misoriented from $\{111\}$ (which is invariably the case), the tendency to continue the surface facet is counteracted by the meniscus angle effect and the changing thermal conditions as the facet extends into or out of the ribbon plane; faceting thus gets relieved by an appropriate transient in the ribbon thickness. In the example shown in Fig. 8a, the surface facet extends into the ribbon (the angle

between the ribbon plane and the facet is $\sim 4^\circ$ as determined by the Sloan Dektak recorder) and is relieved by an increase in ribbon thickness (where the striae reappear). In Fig. 8b, the surface faceting on the (111) plane (near a (111) $[\bar{2}11]$ ribbon seed) is constricted by growth faceting near the periphery on the oblique ($\bar{1}11$) plane.

On occasion, complex faceted features are observed on the ribbon surface, as exemplified in Fig. 9. Region A in the figure is primary-twin related to the original ribbon seed orientation, (100) [011]; regions B and C are both first order twins of region A, hence the boundary between regions B and C is a second order twin boundary. It is interesting to observe that the faceted features are different on the front (Fig. 9a) and back (Fig. 9b) sides of the ribbon. Of course, this is the result of the octahedral planes on which faceted growth occurs having different inclinations relative to the freezing isotherm near the periphery. The example shows that crystallization (and the formation of the external crystal surface) in one region of the crystal occurs independently of any other region. With the orientation in region A being ($\bar{1}22$) $[\bar{4}\bar{1}\bar{1}]$, it appears that faceting is more prevalent on the ($\bar{1}11$) planes at the front of the ribbon than it is on the ($\bar{1}\bar{1}\bar{1}$) planes (which are less inclined to the growth interface) at the back side. A detailed study of the various ridge-like features seen in the figure requires an analysis of the supercooling on the various octahedral planes and of the anisotropic ledge kinetics on these facets. The periodic pattern which is apparent along the second order twin boundary in Fig. 9a (and extends some 15 cm of growth length) is probably the result of a competition between outward growth on the interface facets in the easy $\langle 112 \rangle$ directions and the meniscus angle effect which would tend to contract the ribbon thickness. The changing meniscus angle and shape at the crystal-liquid-vapor triple junction also affect the thermal conditions (i.e., supercooling) at the facet planes.

In general, faceted growth at the ribbon sides has been observed to be very stable; the facets can extend several inches (or, as in the case of the facets in Fig. 7, several feet) along the ribbon length.

Faceting at the ribbon edges

Examples of faceting at the ribbon edges and its effects on the ribbon width are shown in Fig. 10. Figure 10a is the most frequently observed feature; during growth, it is accompanied by a somewhat periodic fluctuation in the meniscus height at the ribbon edge. These fluctuations can usually persist in a stable manner for a short growth length ($\lesssim$ few cm) by which time the growth conditions and crystal orientation (hence the supercooling conditions on the facet planes) may change. As would be expected from the shape stability considerations described above, fluctuations in the shape variables at the ribbon edges are undesirable in that the marginal stability of the ribbon edge (cf. Fig. 3) can be readily upset by these fluctuations. Figure 10b shows a case of edge instability associated with faceted growth; extremely rapid lateral growth here has caused the ribbon edge to almost spread past the edge of the die. Faceting at the ribbon edges, and the fluctuating growth conditions which are generally associated with it, often lead to twin nucleation at the ribbon edges (e.g., Figs. 6 and 10b).

Under unusual growth conditions, faceted growth can lead to extremely stable ribbon edges; an example of this is shown in Fig. 11. Here the ribbon surface orientation is (111) and the growth direction is $[\bar{1}\bar{1}0]$; the ribbon edge has a "lipped" shape (see Fig. 11b) with a $(\bar{1}\bar{1}1)$ surface facet along the outer edge, as shown in the figure. The lip is curved in the opposite direction at the other edge of the ribbon. The ribbon edge was stable for a few cm of growth on one side and nearly 20 cm on the other side; the "stable" growth conditions which were obtained in this growth run could not be consistently reproduced in subsequent trials, however.

In summary, faceted growth is frequently observed in EFG ribbon growth. By far the most important consequence of faceting appears to be that it can override (or, at least, it can compete with) the meniscus angle requirement (i.e., $\phi = \phi_0$) for constant cross-sectional growth. The periodic fluctuations of the faceted features are probably the result of such a competition between the two effects. Similar interactions between faceted and controlled-shape growth have been observed in the growth of rod-shaped crystals and ribbons of germanium by the Stepanov process.⁽⁵⁾ As described above, the tendency for faceted growth is a complex function of the crystal growth conditions such as the growth rate, thermal profiles, impurities, dislocation density, and crystal orientation. Correlations of faceting with the growth conditions in silicon ribbon EFG have not been successful thus far, probably as the result of inhomogeneities in the distribution of dislocations and in the crystallinity of the ribbons. Nevertheless, growth conditions have been achieved where faceting at the ribbon edges (which is, clearly, the primary problem area from the point of view of growth stability) is avoided.

OTHER MORPHOLOGICAL OBSERVATIONS IN EFG RIBBONS

In this section, we examine some morphological features frequently observed in EFG silicon ribbons which are associated with variations or fluctuations in the process variables during growth.

Variations in the edge-defining die dimensions

As described above (also in Ref. 4), mechanical changes in the edge-defining die dimensions occur frequently when graphite dies are used in silicon ribbon EFG (e.g., as a result of SiC particles, die spreading open, mechanical damage or spill-over at die edges, etc.). Figure 12a shows the typical vertical striae seen on the ribbon surface which result from the meniscus wetting around the SiC particles growing at the die top.

Figure 12b illustrates the effect of a spill-over near the edge of the die; the breaks in the striation (denoted by the arrows) were caused by the lateral displacement of the ribbon during growth. In addition to demonstrating the overall stability of the thickness dimension of the ribbon when subjected to perturbations in the die thickness (cf. Fig. 2h), these figures illustrate the effectiveness of the "edge-definition" in EFG. In essence, the ribbon surface is a true reproduction of the actual edge-defining die shape. As the meniscus height increases, the resolution of the die features decreases, as would be expected, and the ribbon surface is smoother.

Variations in meniscus height

The dependence of ribbon thickness on meniscus height for given values of die thickness and h_{eff} (cf. $\phi = \phi_0$ line in Fig. 2a) has been quantitatively verified in silicon ribbon growth experiments⁽⁷⁾. When the meniscus height was purposely changed in the experiments (by changing the crystal pull rate or the temperature gradient in the meniscus film), the ribbon thickness attained a new steady-state value (as depicted in Fig. 2a) following a brief transient period. The same variations in meniscus height at the ribbon edges were generally observed⁽⁷⁾ to lead to an instability (i.e., continued spreading or tapering) of the width dimension of the ribbon.

Localized fluctuations or variations of the meniscus height near faceted regions of the growth interface were described in the preceding section; in these cases, the crystal shape was found to be governed by the detailed kinetics of layer nucleation and growth on the facet planes rather than by a geometrical relationship such as in Eq. (1). Another type of localized variation in meniscus height frequently occurs at the intersection of high angle grain boundaries (e.g., twin boundaries) with the growth interface at the solid-liquid-vapor triple junction. The effect

is probably similar to the grain-boundary grooves in solid-liquid interfaces⁽¹⁴⁾; an example of the resulting surface features in EFG ribbon is shown in Fig. 13. The striae delineate the "groove" at the twin boundary; the surface is slightly depressed (i.e., thickness is less) in this region.

Horizontal surface striae

Many examples of the horizontal striae which are always observed on the surface of EFG ribbons have already been presented, e.g., Figs. 7 and 13. The following observations have been made in relation to these striae: (1) the striae are periodic markers of the growth interface; (2) the striae are parallel, except in regions of local acceleration of growth rate (e.g., start of an interface facet); (3) the striae spacing ($\sim$ few μm) is much greater than the amplitude of the striae; (4) striae on either side of a thin ribbon are "in phase", i.e., the ribbon thickness increases on both sides simultaneously; (5) the striae never cross (i.e., melt back, if any, is much less than the striae-spacing); (6) the striae are not associated with localized variations in impurity or dopant concentration in the ribbon; (7) the striae-frequency is independent of the suspended length of the ribbon, of the puller mechanism, and of the frequency of the furnace power supply (60 Hz, 9.6 kHz and 450 kHz); (8) the striae frequency has been observed to vary from 0 (near the seed where the crystal growth rate is low) to ~ 150 Hz at the fastest ribbon growth rates achieved thus far (~ 5 cm/min). There is some evidence that the striae frequency is, in fact, roughly proportional to the growth rate. Further work is in progress to identify the mechanism of the striae formation; it appears to be associated with transient variations of the process variables in Eq. (1). A recent analysis⁽¹⁵⁾ of the time-dependence of perturbations in the geometrical variables in the floating zone process showed an oscillatory behavior for that system; the frequency of the oscillations was found to be proportional to the ratio of the growth rate to the length of the molten zone.

Interface breakdown

In EFG ribbons produced under low gradient, high growth rate conditions (e.g., near the maximum growth rate, which is a function of the thermal environment of the growth setup), we have observed various morphological features which indicate interfacial breakdown phenomena. These features usually take the form of corrugated, dendritic patterns, or wavy surface ridges such as illustrated in Fig. 14. These ridge-patterns appear on both sides of the ribbon (nearly simultaneously) and tend to be somewhat symmetrical about the ribbon axis (this is not the case in the example shown in Fig. 14). Analyses have shown that the interfacial breakdown is caused by thermal and/or constitutional supercooling, as described in detail elsewhere⁽¹⁶⁾.

CONCLUSIONS

1. Silicon ribbon growth by the EFG process has been shown to occur under one or both of the following conditions: (i) controlled-shape growth, where the ribbon shape is determined by the shape of the meniscus at the crystal-liquid-vapor triple junction (i.e., $\phi = \phi_0$ for steady-state cross-sectional growth) and hence by the geometrical process variables (t_d , h_{eff} and s in Eq. (1)); or (ii) faceted growth, where the external shape of the crystal is determined by the detailed kinetics of ledge nucleation and growth on peripheral $\{111\}$ facets.

2. Theoretical analysis of the ribbon shape stability for controlled-shape growth has shown that the side of the ribbon (i.e., the thickness dimension) is inherently stable, whereas the ribbon edge (i.e., the width dimension) is only conditionally stable when a steady-state growth system is subjected to perturbations in the geometrical variables. The stability of

the ribbon edge requires that the edge-defining die radius should not exceed approximately twice the radius of curvature of the ribbon at the ribbon edge. Experimental evidence has been presented to show the inherent stability of the ribbon side and the relative instability of the ribbon edges.

3. The characteristic meniscus angle φ_0 for the growth of a constant-dimension crystal in controlled-shape growth has been shown to depend on the crystallographic orientation of the ribbon surface. Observations of ribbon thickness changes which resulted from the φ_0 -anisotropy were used to obtain a measure of the anisotropy in the crystal-vapor surface free energy in silicon.

4. Faceted growth has been shown to compete with, and, on occasion, completely override controlled-shape growth. If the surface shape in a given region of the ribbon is the result of faceted growth, then the $\varphi = \varphi_0$ condition does not apply in this region.

5. Faceted growth and φ_0 -anisotropy did not affect the stability of the ribbon side (i.e., thickness), but were generally observed to lead to instabilities at the ribbon edges (i.e., spreading or tapering of the width dimension).

6. Experiments with various ribbon seed orientations were carried out to obtain the various φ_0 -anisotropy and faceting features reported in this paper. Irrespective of the seed orientation, an equilibrium defect structure eventually developed in the ribbons; the orientation was approximately $(110)[\bar{1}12]$ and the ribbons contained a high density of linear boundaries parallel to the growth direction. An example of this structure is shown in Fig. 15; the edge-stability where the linear boundaries extend to very near the ribbon edge (indicated by the oblique arrow) should be noted. Further analysis of this equilibrium defect structure is given in a separate publication⁽¹¹⁾.

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REFERENCES

1. H. E. Bates, F. H. Cocks, and A. I. Mlavsky, Proc. Ninth IEEE Photovoltaic Specialists Conf., p. 386, IEEE, New York (1972); H. E. Bates, D. N. Jewett, and V. E. White, Proc. Tenth IEEE Photovoltaic Specialists Conf., p. 197, IEEE, New York (1974).
2. T. F. Ciszek and G. H. Schwuttke, Phys. Status Solidi (a), 27, 231 (1975).
3. J. C. Swartz, T. Surek, and B. Chalmers, J. Electron. Mater., 4, 255 (1975).
4. K. V. Ravi, H. B. Serreze, H. E. Bates, A. D. Morrison, D. N. Jewett, and J. C. T. Ho, Proc. Eleventh IEEE Photovoltaic Specialists Conf., p. 280, IEEE, New York (1975).
5. P. I. Antonov, J. Cryst. Growth, 23, 318 (1974).
6. T. Surek and B. Chalmers, J. Cryst. Growth, 29, 1 (1975).
7. D. A. Yates and T. Surek, Paper 138 presented at The Electrochemical Society Meeting, Washington, D. C., May 2-7, 1976.
8. T. Surek, Mobil Tyco Solar Energy Corp., submitted for publication.
9. J. A. Champion, B. J. Keene, and S. Allen, J. Mater. Sci., 8, 423 (1973).
10. W. Bardsley, F. C. Frank, G. W. Green, and D. T. J. Hurle, J. Cryst. Growth, 23, 341 (1974).
11. L. C. Garone, C. V. H. Rao, A. D. Morrison, T. Surek, and K. V. Ravi, Mobil Tyco Solar Energy Corp., submitted for publication.
12. M. G. Milvidskii and A. V. Berkova, Sov. Phys. Solid State, 5, 374 (1963).
13. T. F. Ciszek, J. Cryst. Growth, 10, 263 (1971).

14. R. J. Schaefer, M. E. Glicksman, and J. D. Ayers, *Phil. Mag.*, **32**, 725 (1975).
15. T. Surek and S. R. Coriell, Paper 140 presented at The Electrochemical Society Meeting, Washington, D. C., May 2-7, 1976.
16. J. C. Swartz, Mobil Tyco Solar Energy Corp., unpublished research (1976).

Table I. Changes in Ribbon Surface Elevation Caused by the Anisotropy in ϕ_0 .

<u>Orientation Change</u>	<u>No. of Tracings</u>	<u>Avg. Elevation Change (μm)</u>	<u>Avg. Transient Distance (mm)</u>
(111) $[\bar{1}\bar{1}0]$ to (511) $[\bar{1}\bar{1}4]$ or to (151) $[\bar{1}\bar{1}4]$	22	7.7 ± 3.0	0.2 to 0.6
(111) $[\bar{2}\bar{1}1]$ to (151) $[\bar{2}\bar{1}7]$	7	9.0 ± 2.2	0.3 to 0.8
(110) $[\bar{1}\bar{1}1]$ to $(\bar{1}\bar{1}4)$ $[5\bar{1}1]$	2	1.5 ± 0.7	0.2 to 0.4
(100) $[001]$ to (122) $[2\bar{2}1]$	3	-1.5 ± 0.4	0.1 to 0.5
(110) $[\bar{1}\bar{1}0]$ to (110) $[\bar{1}\bar{1}4]$	3	1.8 ± 0.9	0.2 to 0.5
(110) $[\bar{1}\bar{1}1]$ to (110) $[\bar{1}\bar{1}5]$	6	3.3 ± 1.2	0.3 to 0.8

Fig. 1. Schematic illustration of ribbon growth by the EFG process showing the geometrical variables which determine the ribbon shape.

Fig. 2. Meniscus height-ribbon thickness curves in silicon ribbon EFG for various values of die thickness, meniscus angle and h_{eff} , and analysis of perturbations in the geometrical variables. (a) Perturbation in meniscus height; the steady-state ($\phi = \phi_0$) and non-steady-state ($\phi < \phi_0$ and $\phi > \phi_0$) curves were calculated for $\phi = 11^\circ, 0^\circ$ and 20° , respectively. (b) Perturbation in die thickness; $\phi = 20^\circ$ for the non-steady-state curve for t_{d2} . (c) Perturbation in h_{eff} ; $\phi_0 = 11^\circ$. (d) Perturbation in meniscus angle; $\phi_0^1 = 11^\circ$ and $\phi_0^2 = 5^\circ$.

Fig. 3. (a) Variation of $t/2$ at ribbon end with meniscus height for various values of the meniscus angle and $h_{eff} = 2$ cm. The non-steady-state curves ($\phi \neq \phi_0$) are shown schematically. The steady-state point A is stable, while point D is unstable when the meniscus height is perturbed. (b) Perturbation in the edge-defining die radius ($t_d/2$). The $\phi > \phi_0$ curve for t_{d2} is shown schematically.

(a)

(b)

Fig. 4. Examples of twins in EFG silicon ribbon which lead to changes in steady-state ribbon thickness as a result of the ϕ_0 -anisotropy. (a) Surface orientation changes from $\{111\}$ to $\{115\}$ to $\{111\}$ to $\{115\}$ for regions A to D, respectively. (b) Surface orientation changes from $\{100\}$ to $\{122\}$ to $\{100\}$ to $\{122\}$ for regions A to D, respectively. The arrow denotes the crystal growth direction (g.d.)

(a)

(b)

(c)

Fig. 5. Perturbations in the width dimension of EFG ribbons when a twin or other high angle boundary emerges at the ribbon edge (shown by the arrows). The crystal growth direction is from top to bottom in the photographs.

Fig. 6. Fluctuations in ribbon width accompanying the nucleation of many high angle grain boundaries. The arrow denotes the crystal growth direction.

Fig. 7. Growth faceting at a twin boundary in silicon ribbon EFG. The surface striae delineate the shape of the solid-liquid interface (shown in the sketch) during growth.

(a)

(b)

Fig. 8. Surface facets (specular $\{111\}$ faces) on the side faces of EFG ribbons grown with a nearly $\{111\}$ surface orientation.

(a)

(b)

Fig. 9. Complex growth facets observed on the front (a) and back (b) sides of an EFG ribbon seeded in the $(100) [011]$ orientation. The figure demonstrates that crystallization (and the formation of external surface features) occurs in various regions of the ribbon independent of any other region.

(a)

(b)

Fig. 10. Growth faceting at the edges of EFG ribbons: (a) Faceting accompanied by nearly periodic fluctuations in meniscus height at the ribbon edge (the ribbon orientation is approximately $(231) [\bar{3}13]$ near the edge); (b) Edge instability caused by rapid lateral growth on peripheral facets. The arrow shows a small, specular surface facet at the ribbon edge.

Fig. 11. Side (a) and cross-sectional (b) views of "lipped" ribbon; faceting at the ribbon edges has resulted in extremely stable growth in this case.

Fig. 12. (a) Vertical striae on EFG silicon ribbon caused by SiC particles which grow at the die top. (b) Thick ($\sim 1 \text{ mm} \times 1 \text{ mm}$) striation on ribbon surface caused by spill-over near one edge of die. The ribbon was moved sideways where indicated by the arrows.

Fig. 13. Groove in growth interface at its intersection with a twin boundary in silicon ribbon EFG showing slight depression in the crystal surface at the groove.

Fig. 14. Wavy surface ridges on EFG ribbon resulting from interfacial breakdown.
The growth rate was 5 cm/min.

Fig. 15. Etched segment of EFG ribbon showing equilibrium defect structure. The orientation is approximately $(110) [\bar{1}12]$. The oblique arrow denotes one edge of the ribbon.