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THICK FILM SILICON GROWTH TECHNIQUES

by

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(NASA-CR-131601) THICK SILICON GROWTH TECHNIQUES Quarterly Progress Report, 1 Dec. 1972 - 28 Feb. 1973 (Tyco Labs., Inc.) 29 p HC $3.50 CSCL 20B

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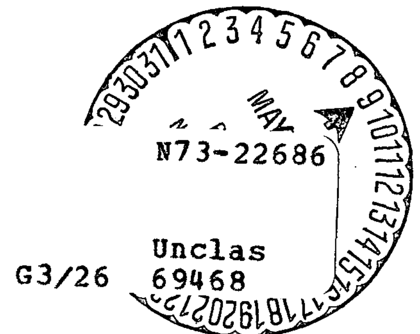

Fourth Quarterly Progress Report
Subcontract No. 953365
Covering Period: 1 December 1972 - 28 February 1973

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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ABSTRACT

Hall mobility measurements on a number of single crystal silicon ribbons grown from graphite dies have shown some ribbons to have mobilities consistent with their resistivities. The behavior of other ribbons appears to be explained by the introduction of impurities of the opposite sign. Growth of a small single crystal silicon ribbon has been achieved from a beryllia dia. Residual internal stresses of the order of 7 to 18,000 psi have been determined to exist in some silicon ribbon, particularly those grown at rates in excess of 1 in./min. Growth experiments have continued toward definition of a configuration and paremeters to provide a reasonable yield of single crystal ribbons. High vacuum outgassing of graphite dies and evacuation and backfilling of growth chambers have provided significant improvements in surface quality of ribbons grown from graphite dies.

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I. SUMMARY

Measurements of the Hall mobility of holes in a number of p-type silicon ribbons grown from graphite dies have shown that some of the ribbons have carrier mobilities consistent with their resistivities. For example, three closely grouped samples had an average mobility of 300 cm^2/V-sec and an average resistivity of 0.5 Ω-cm. This mobility is typical of single crystal silicon, singly-doped to this resistivity level. Other samples appeared grouped in a pattern indicative of the introduction of varying amounts of a compensating n-type impurity, resulting in increased resistivity and lowered mobility. High vacuum outgassing of graphite dies and vacuum purging of the growth apparatus have contributed to improved surface quality and cleanliness of the silicon ribbons grown recently. Investigations of the role of various growth parameters and setup configurations have continued with the goal of elucidating and controlling those variables which influence ribbon quality and yield. Recently, growth of a single crystal ribbon from a beryllia die was achieved; although not completely evaluated yet, this is an encouraging result.

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II. INTRODUCTION

One primary limitation to the large-scale use of silicon solar cells in generating electric power from sunlight has been the lack of an industrially feasible process for the growth of single crystal silicon ribbons directly and continuously from the melt. Edge-defined, film-fed growth (EFG) is a process by which single crystals may be grown with their shape controlled by the outside dimensions of a die, the growth actually occurring through a thin liquid film on the top surface of the die.[1-5] The EFG method overcomes the need for refined temperature control during growth which characterized other attempts at the growth of ribbon-shaped crystals. However, the process imposes stringent requirements on the nature of the die material if semiconductor quality crystals are to be grown.

Fig. 1 illustrates the application of the EFG method to the growth of a ribbon-shaped crystal. When the crucible and melt are heated to above the melting point of silicon, the liquid silicon rises to fill the feeding slot by capillary action. A silicon seed crystal is then brought into contact with the liquid silicon in the capillary seed slot. After adjustment of the melt temperature and seed withdrawal rate, the molten silicon spreads across the top of the die until the spreading of the liquid silicon is halted by the 90° change in effective contact angle at the outer perimeter. The growth of a silicon crystal ribbon from the thin liquid meniscus shown in Fig. 1 is then established. This method has been applied to the growth of ribbons, filaments, tubes, and other shapes of sapphire, barium magnesium titanate, lithium fluoride, copper-gold alloy crystals, and beta-alumina, as well as to the directional solidification of a variety of eutectic materials.

The basic features of the EFG technique can be summarized as follows:

1. It produces accurately controlled cross sections and, in particular, thin ribbons can be produced directly.

2. It is self-stabilizing over a relatively wide range of power input fluctuations by means of changes in the thickness of molten film, or meniscus.

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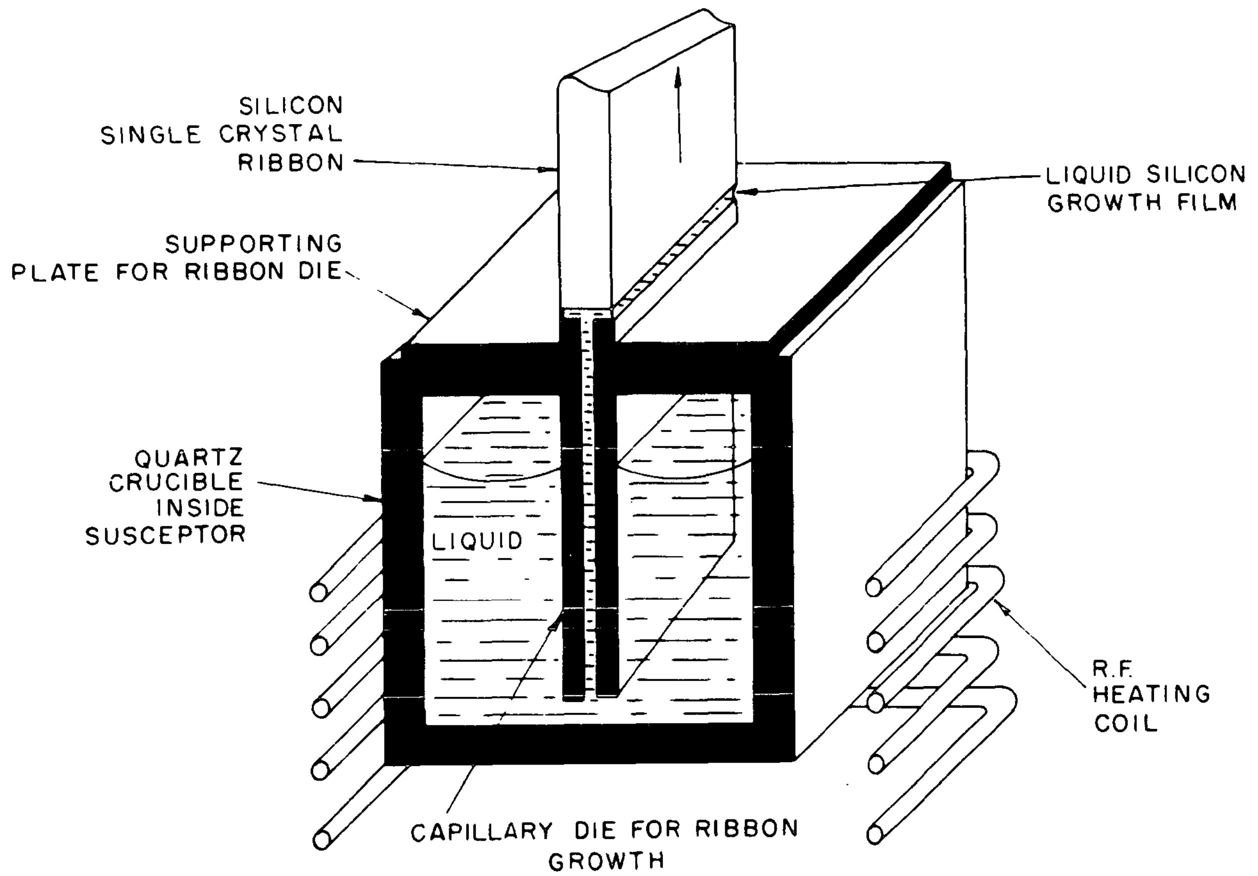

Fig. 1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon

3. Growth rates can be very fast since they are limited only by latent heat removal from the solid-liquid interface.

4. The growth interface is effectively decoupled from the bulk melt surface, permitting continuous replenishment of the melt during growth.

5. The crystal orientation can be arbitrarily chosen.

6. Because of the fast growth rate and the faster linear motion rate of the liquid supply, segregation effects tend to be completely overcome, and the crystallizing solid has the same average composition as the bulk liquid.

7. The steep thermal gradient between the growth interface and the die prevents the breakdown of planar growth. Thus, crystal perfection is enhanced and cellular substracture suppressed.

In the following sections of this report, we discuss the progress which has been made to date in applying this method to the thick film silicon ribbon growth.

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III. TECHNICAL DISCUSSION

A. Silicon Ribbon Growth Results

1. Growth experiments

Growth experiments have continued with the goal of defining the parameters and physical configurations appropriate to the growth of single crystal silicon ribbons. We have at least four somewhat interrelated problems to deal with, all of which are essentially a function of controlling the heat flow(s) around the orifice so that the temperature is uniform along the length of the orifice. The problems at present are:

1. The liquid zone/meniscus is probably too thin, and this allows minor perturbations in the underlying solid, as might be caused by SiC precipitates, to unduly influence the shape of the freezing interface thereby nucleating new grains;

2. The meniscus is not uniform in thickness which means that (1) is exaggerated in places;

3. The temperature is not uniform across the orifice, which is basically the cause of (2) but also means that to initiate spreading of the freezing interface from the seed the average temperature of the setup must be lowered excessively; and

4. Operation of processes (1) and (2) can produce poor surfaces by furrowing (misshapen interface) and pickup of SiC crystallites which are frozen into the surface.

What has to be accomplished, then, to correct these problems is to provide a level temperature gradient across the orifice and to decrease somewhat the vertical temperature gradient immediately above the orifice.

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It is to achieve these results that we have conducted a number of experiments to examine the effect of position of the orifice relative to the top of the die holding plate (lid). Over a range of orifice heights it was found that with the orifice low, the end of the orifice would be too hot, thereby preventing growth at the full width. This is not an unexpected result, since the basic characteristic of the setup is for the ends of the orifice to be hotter than the center as they are closer to the walls of the susceptor, whence the heat flows. The higher positions for the orifice results in a smaller center-to-end temperature differential, but here the problem of steep vertical gradients results in a very thin meniscus with its attendant problems. The curved orifice should provide a partial solution to these problems. In principle, there is a radius of curvature of the orifice which will closely follow the desired isotherms when positioned at the proper height. In practice we have found that curved orifices do not perform significantly better than flat orifices, with the exception of during the spreading phase, when a curved orifice will usually require a much smaller temperature excursion to spread the freezing interface.

One of the basic features of the growth process which has heretofore been difficult for us to manipulate is the shape of the freezing interface. We feel that this can be of considerable importance to the quality of the ribbons, yet generally the interface has been concave (with respect to the liquid zone) or very nearly flat. Only in ribbons substantially less than the full width of the orifice have we seen convex interfaces; and the yield of single crystals is significantly greater in this class of ribbons than in those of full width. At first glance it would seem that this should be a simple condition to obtain, since the ends of the orifice tend naturally to be hotter than the center. Our observations on full width ribbons, however, are that during growth the ends are always cold, probably as a result of radiation from the edges of the ribbon. Thus, we have to provide a 1-cm wide ribbon with a similar environment to that of a narrow ribbon. One approach which we will try is to increase the diameter of the setup to approximate the width/diameter relationship which a narrow ribbon currently experiences. Alternatively, the spread of the freezing interface can be limited to the midsection of a wider orifice.

2. Ribbon surfaces

In general, the surfaces of the majority of ribbons grown recently are smoother and cleaner than the average ribbons grown earlier in the development of graphite dies. There seems to be some correlation between this improvement in

surface quality and evacuation and backfilling of the growth chamber. This step was recently instituted and seemed to result in a marked decrease in the amount of SiC precipitated in and around the meniscus. Apparently the residual air in the setup, prior to evacuation, acted to catalyze, or in some way increase the extent of, reaction between the melt and the die.

3. Electrical properties

a. Carrier mobility measurements

Several months ago results of mobility measurements on Hall samples from two ribbons were reported (Third Quarterly Report). The measured mobilities were very low, while the apparent bulk resistivities were fairly high (50 and 10 Ω-cm). These results were attributed to poor sample preparation or possibly very imperfect material. The samples were, in fact, quite small and could have been deeply damaged; in light of recent results, it may be that the interpretation was incorrect. It was clear, however, that the preparation of tiny Hall bars from thin ribbons was a very tedious process, ignoring the doubt it cast on the results. This led us to experiment with the van der Pauw[6] method for measurement of the resistivity and Hall mobility. Sample preparation and contacting are much less fussy than Hall specimens. Our initial results on samples from a float-zoned ingot were in line with predicted values, and repeated measurements on the same sample demonstrated reasonable precision.

Our van der Pauw samples are prepared by scribing the ribbon and breaking a piece out approximately as long as the ribbon is wide, sawing part-way along the diagonals from each corner with a diamond saw and then etching to remove the damaged material. This results in a roughly cruciform sample with a central section approximately 0.2 in. square. Contacts are prepared by sandblasting a small area at the edge of each arm of the cross. This area is then coated with a colloidal carbon slurry which is allowed to dry; then a coating of colloidal silver paint is applied over the carbon. The lead wires are coated with silver paint at the same time and allowed to dry in place, immersed in the silver paint on the contact. These contacts are simple to make and quite reproducible and ohmic.

Measurements were made using dry cells as a current source, a Fluke Model 825A Differential DC Voltmeter, and fixed resistors in series with the sample to measure the current. Magnetic field strength was 11.6 to 11.8 kilogauss. All measurements thus far have been at room temperature.

Our initial measurements were a series of repeated measurements on two samples from a p-type float-zoned ingot of approximately 62 Ω-cm nominal resistivity to establish a feel for the precision of our technique. The results for seven measurements on four sets of contacts were: resistivity, 54.6 ± 7.7 Ω-cm; mobility, 360 ± 25 cm^2/V-sec, where the ± values are computed standard deviations. Here the four sets of contacts are considered to be the independent measurements, so that these figures presumably represent systematic errors in the deviations of the averages from the "true" values of the quantities, while the standard deviations represent the precision of the measurement technique – mainly, presumably, the reproducibility of the contacts and the precision of measurement of the sample thickness. The internal precision of making a given measurement, i.e., for a set of contacts appears to be about ± 1%. This is a fairly limited sample from which to make any solid statistical deductions, but initially it would seem that we have a systematic error giving values about 10% too low for both resistivity and mobility, and measurement errors of approximately 14% for the resistivity and 7% for the mobility.

Table I lists the results of measurements on eight silicon ribbons grown from graphite dies. Also included in the table are the results of previous measurements on rectangular Hall samples from two ribbons, one of which has also been measured by the van der Pauw method, and the average values determined for the single crystal, float-zoned material. The literature values are taken from the curve drawn by Runyan[7] through the data of a number of investigators, mainly for boron-doped silicon. This curve and the data of Table I are also shown in Fig. 2, which indicates clearly that the ribbons characterized thus far fall into three categories: (1) mobility appropriate for the resistivity (carrier concentration), (2) mobility down by 30 to 40% from that commensurate with the resistivity, and (3) resistivity substantially higher than other ribbons, but mobility very low. We interpret these results as being indicative in the first case of addition of a single fully ionized p-type impurity (probably Al) from the quartz crucible. The second group would appear to have achieved its slightly higher resistivity by a slight degree of compensation which has produced material with a mobility characteristic of a somewhat greater impurity concentration, but which is belied by the higher resistivity. It should be noted here that an underlying assumption to these explanations is that, all things being equal, we would expect all material grown as these samples have been to exhibit a fairly characteristic resistivity of about 0.5 Ω-cm as a result of contamination by a dominant impurity source, probably the crucible, but possibly the die. Operation of this mechanism would

Table I. Room Temperature Hall Mobilities of P-Type Silicon Ribbons Grown from Graphite Dies

Sample	Resistivity (Ω-cm)	Mobility: Measured (cm^2/V sec)	Mobility: From Literature (cm^2/V sec)
73 A	0.6	160	310
75 A-1	23.9	20	400
75 A-2	56	15	410
75 C	1.5	195	350
76	0.4	335	290
106	12.8	20	395
117	0.6	295	310
118 A	0.8	190	325
124	0.6	270	310
Float zone	54.6	360	410
72	50	10	410
75 C	10	10	390

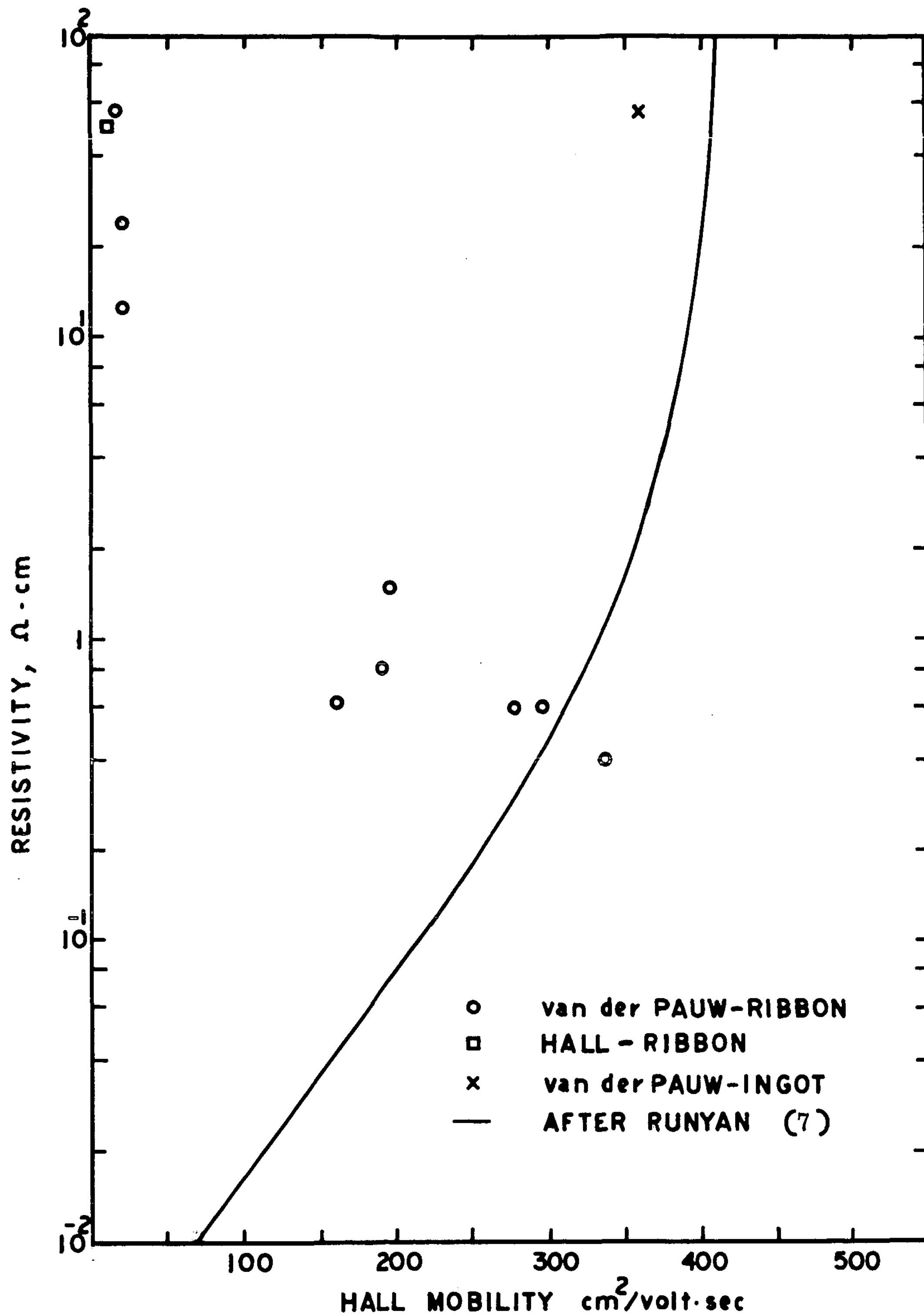

Fig. 2. Hole mobilities as a function of resistivity for a number of silicon ribbons grown from graphite dies (The point, x, represents a single crystal, float-zoned ingot used as feed material for ribbon growths)

produce ribbons in the first category. Introduction of greater or lesser amounts of an n-type impurity would then be expected to yield material of the sort found in the other categories.

There is some internal evidence in support of these ideas. Ribbons 75 A and 75 C were grown from the same die and melt. Fortuitous contamination of the melt to yield material typical of 75 A would be expected to mix sufficiently to yield similar properties in a subsequent ribbon; however, 75 C is significantly different. If, however, one assumes a limited source of a compensating impurity in the die (where the molten silicon is exposed to it in a sequential fashion), then it is likely that the first ribbon grown would be like 75 A. As the source of impurity is depleted by growth of more material, then the ribbon will come to nearly resemble "typical" melt material, that is, something less than 1 Ω-cm and mobility approaching that for material with a (single) ionized impurity type. The die for 75 was vacuum outgassed at about 10 μ and 1300°C for a short time. This was a much less thorough outgassing than subsequent dies received and it is possibly the reason for the behavior of the ribbons grown from the die as contrasted with later runs.

The relative simplicity of measurements by the van der Pauw method and the significant information to be obtained point to its considerable utility as a diagnostic tool in identifying sources of contamination in the ribbon growth process, and in following the progress made in eliminating them.

b. Resistivity

The resistivities listed in Table I are those determined by the van der Pauw method. These values have shown considerably more consistency and accuracy than our previous measurements using a four-point probe. For example, measurement of the resistivity of one ribbon (C-124) by means of six contacts of the same type as used on van der Pauw samples yielded the same value as was subsequently determined from the small samples. Similarly, reasonable agreement was obtained with the manufacturer's reported resistivity for samples from a float-zoned ingot.

It appears that at least some of the high resistivities measured earlier are real, as confirmed by Hall and van der Pauw measurements. Indeed, there is no reason not to believe all of them, but it also appears now that they were all due to varying degrees of fortuitous compensation by die contaminants. With increasing thoroughness in die bakeout, from $> 10^{-3}$ to 10^{-5} mm Hg vacua, and increased

temperatures, presumably the tendency toward a rather uniform 0.5 to 1.0 Ω-cm resistivity lately observed is, as noted above, the result of "unmasking" of a uniform source of $\sim 5 \times 10^{16}$ cm^{-1} acceptors.

We have just completed a two-point probe apparatus where current will be passed into the sample through carbon/silver point contacts and the probes will measure the voltage gradient along the ribbon. We expect that with this technique, more reliable results will be obtained. However, the van der Pauw method will probably become the mainstay of our electrical characterization.

4. Internal stress in silicon ribbons

Since we began successfully growing silicon ribbons from graphite dies, several ribbons have split longitudinally during handling after growth. If the fracture does not run out of the ribbon, the split halves are observed to exhibit a greater or lesser curvature away from the centerline of the ribbon. This is taken to indicate the presence of residual internal stresses which have been released by the propagation of a crack. It can be readily demonstrated that the presence of non-uniform gradients across the growth interface region in EFG can result in residual stress in a ribbon. Hurley and Pollock[8] developed, for sapphire ribbons, a model and equations to calculate stresses in a ribbon prior to splitting. Their model assumes that the stress across the width of a ribbon varies linearly from a maximum tensile value at both edges to a maximum compressive value at the center, and is symmetrical about the zero stress level. This model is in qualitative agreement with the observed curvature in silicon, sapphire, and other oxide ribbons.

We have measured the separation between the halves of four split ribbons and, assuming uniform curvature, used Hurley's equation to calculate the residual stress in the ribbons. The results are listed in Table II. There appears to be some correlation with growth rate which is not unexpected. For a given afterheater length and temperature profile, there is a limiting growth rate, above which the ribbon is not able to cool uniformly as it is continuously moving into an increasingly colder environment. The "cooling down" of a ribbon, if it proceeds too rapidly, becomes a quenching process in which gradients are established within the ribbon as a result of the limits on heat conduction within the ribbon. These temperature gradients can then produce size mismatch within the cooling piece which must be accommodated by flow of the softer (higher temperature) material. The upper limit of the residual stress, which can be produced by such a process, is the yield strength at the temperature at which the deformation (accommodation) occurs. Runyan[7] presents a plot of

Table II. Calculated Internal Stresses in Split Silicon Ribbons Grown from Graphite Dies

Ribbon	Thickness (in.)	Growth Rate (in./hr)	Internal Stress (psi)
C-62	0.019	90	17,200
C-80	0.024	50	7,900
C-86 B	0.020	~60	8,700
C-115 B	0.012	70	16,700

ultimate tensile strength of silicon as a function of temperature. The tensile strength in the region of 1250° to 1400°C is approximately 16,000 psi, which indicates that our values of residual stress are approximately correct. (The yield stress is less than the ultimate tensile strength, but not significantly so in silicon). Our residual stress values also indicate that the system from which the ribbons were grown was barely adequate to provide a proper cooling rate when the ribbons were grown at speeds approaching 1 in./min. At higher growth rates, clearly the ribbons were subjected to cooling rates which produced stresses equal to the yield strength.

This provides us with a means to gauge the adequacy of any afterheater design, since it is possible to deliberately initiate splitting in a ribbon which is suspected of having residual stress. Inspection of ribbons under crossed infrared polarizers can reveal the existence of residual stress, but gives no quantitative information, unless it was possible to correlate the width of the apparent strained areas with subsequent values of stress calculated from splitting.

B. Beryllium Oxide Dies

After establishing the essentially non-wetting behavior of Si with beryllia (Third Quarterly Report) and the ability of a carbon coating to provide temporary wetting, it was necessary to establish the ability of such carbon coatings to "pull" a Si column up a capillary slot in BeO. This was done, and then subsequently a liquid Si column was maintained in a simulated BeO die feed slot for over an hour. The slot was $0.7 \times 0.28 \times 0.020$ in. Again, a coating of colloidal graphite was applied to the inner surfaces of the slot to promote the initial rise. At this point we decided to proceed with procurement of proper dies fabricated from BeO.

Dies, identical in configuration to our graphite dies, were fabricated from Brush-Wellman Thermalox® 995, a 95% dense, pressed, and sintered material. The major impurity in this material (other than SiO_2 at about 0.3%) is MgO, present at about 0.2%. Higher purity material is available.

Thus far, two growth experiments have been run with BeO dies. Conventional growth setups were used. The dies were vacuum outgassed after coating of the feed slots with colloidal graphite. A normal argon/5% hydrogen atmosphere was used during the experiments. The feed slots of both dies filled readily and maintained their columns of liquid silicon for over 90 min. Mechanical problems prevented any significant growth in the first experiment. Two narrow ribbons were grown from the second. One was approximately 6 in. long with a maximum width of 0.150 in.; the

other was approximately 0.170 in. wide by 3 in. long. Growth rates were approximately 50 in./hr. Neither ribbon has been fully characterized yet, although the longer of the two is single crystalline.

Some difficulty was experienced in maintaining sufficient heat input to the BeO dies to maintain growth conditions during the experiments. It would appear that this is due to the thermal properties of BeO being sufficiently different from graphite that some modifications to the shielding are necessary. We are currently fabricating appropriate lids and shields to maintain more suitable thermal conditions at the orifice for the remaining tests of BeO dies.

IV. CONCLUSIONS AND RECOMMENDATIONS

The most significant finding of this period was that it is possible to achieve reasonable carrier mobilities in silicon grown from graphite dies. While it seems that we still have to locate and eliminate other sources of impurities, once this is accomplished we will be able to grow material with adequate and controllable properties for solar cells.

During the next quarter our efforts will be directed toward: (1) continued development of graphite dies and associated technology, (2) elimination of active impurity sources within the system, (3) continue investigation of BeO orifices, and (4) continued investigation of the compatability of other refractory materials with liquid silicon.

V. NEW TECHNOLOGY

No new developments are to be reported during this contracting period.

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