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LARGE AREA SILICON SHEET BY EFG

Program Manager: F.V. Wald

Annual Progress Report - Subcontract No. 954355

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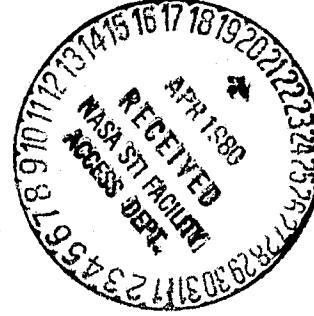
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ABSTRACT

The present annual report details the considerable progress which has been made in 1978/1979 to evolve systems designs for growth stations which produce multiple silicon ribbons by the EFG process.

This progress culminated in the demonstration of five ribbon multiple growth in May 1979 and in recent advances toward improved electronic quality of ribbons grown from these machines.

These advances were made in large measure by studies in which the composition of the gas environment around the meniscus area was varied. By introducing gases such as CO_2, CO, and CH_4 into this region, reproducible increases in diffusion length and cell performance have been realized, with the best large area (5 cm x 10 cm) cells exceeding 11% (AM1) efficiency.

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Table of Contents

List of Figures

List of Tables

ERRATUM

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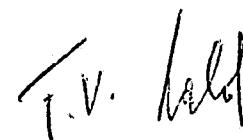
F. V. Wald
Program Manager

I. INTRODUCTION

The signal success of the five ribbon multiple run in May 1979, which produced from five cartridges 150 m of 5 cm wide ribbon with an average growth speed of ~3.5 cm/min at a machine duty cycle over 90%, has now clearly demonstrated that "cartridge type" multiple EFG machines can be considered "prototypical" for the development of the future production equipment with which to fabricate silicon ribbon base material at the low costs necessary to achieve the 1986 LSA project goals.

Upscaling of the cartridge to the ultimate 10 cm width which, at growth speeds below 5 cm/min, is considered necessary to achieve the final cost goals, is also well underway, along with the development of a viable automatic control system which at this point appears to be sufficiently advanced and also sufficiently inexpensive, to allow perhaps more than the originally projected ten ribbons to be under the control of a single machine operator.

The program has thus made great strides in arriving at a scalable production technology for multiple EFG ribbons, and it appears that in the coming year conclusive final design choices for a production unit will become possible.

Also, in the five ribbon multiple run, it was demonstrated that material from such units can indeed have reasonable electronic properties, since large area (~50 cm^2) cells of ~9% efficiency could be prepared from silicon ribbon grown in that experiment.

Such efficiencies, although significant as a general demonstration that this type of equipment in principle can produce ribbon with acceptable electronic properties, are not considered sufficient to meet the LSA project goals for 1986.

Hence, very significant efforts in this program were directed toward the identification and study of mechanisms which could optimize or

1

degrade the electronic properties of the ribbon during growth as well as during processing into solar cells, and these studies will be further emphasized during the coming year.

So far as crystal growth is concerned, the work has focused on an examination of material quality changes arising from variations in die design, construction materials, thermal conditions and the furnace ambient.

Although we consider optimized die designs and thermal conditions to be worthy of further study, and of importance in particular as they allow us to influence the meniscus height during growth which appears to be a significant variable, it was the furnace ambient manipulation which has led to reproducible, unambiguous, and positive changes in growth system behavior and material quality, such that a definite breakout in solar cell performance over earlier baseline levels in these machines has been observed.

From these experiments, large area (50 cm^2) cells of 11.5% (AM1) efficiency have now resulted, and it is believed that optimization of the gas ambient in the furnace and particularly around the meniscus will lead to further efficiency increases. At this point, it is realized that the gas ambient, in particular with respect to carbon and/or oxygen containing species such as CO, CO_2, and CH_4, was perhaps the one most important unrecognized and uncontrolled parameter affecting growth and properties of EFG silicon ribbon prepared from carbon dies.

However, a distinct model linking ribbon properties and gas phase composition, flow, etc., must now be evolved and proven, and subsequently the results must be applied in appropriately designed machines which control and optimize the relevant parameters. Therefore, because of the apparent importance of the observations so far, we plan to devote a very significant effort to these questions in the year ahead.

Finally, it has become clear that solar cell fabrication sequences can have a significant influence on the material properties in the final cell through the high temperature processing now commonly associated with cell fabrication. It is also suggested that such influences can be both positive or negative, i.e., the diffusion length may decrease during processing, or, through such mechanisms as gettering, precipitation, or complexing, it may perhaps be made to increase.

In either case, the development of processing sequences which at least conserve, and hopefully could improve the initial minority carrier

2

lifetime of imperfect materials, such as EFG ribbon, can conceivably have a large influence on the final solar cell efficiency. These questions, therefore, will continue to be explored. However, at this point in time, multiple EFG ribbon technology appears to be extremely well placed toward actual achievement of the 1986 LSA program goals.

II. WORK ON CRYSTAL GROWTH STATION NO. 1 by J.P. Kalejs

A. Overview

The study of the effects of system component design and growth
parameter variation on ribbon quality has been continued during the
course of experiments carried out in JPL No. 1 in the past year. Sig-
nificant improvements in levels of SPV diffusion lengths and solar cell
efficiencies have been realized in this time. As a result, peak SPV
values now have reached a range of 40 to 60 μm, and solar cell efficien-
cies over 11% (AM1 and AR coated) have been demonstrated in large area
($\sim$50 cm^2) cells.

A basically empirical approach to quality studies has been adopted,
necessitated to a great extent by the complexity of the growth system
and interdependence among many available variables. The past year's
work has focused on an examination of system responses and material
quality changes arising from variations in die design, from interchange
of components of different materials of construction (graphite vs.
molybdenum), from growth with and without a cold shoe, and from deliber-
ate furnace ambient manipulation. Only the latter has led to unambiguous
and reproducible changes in growth system behavior and material quality,
and has been associated with a breakout of peak performance levels from
the baseline established in earlier experiments.[1,2]

Ambient changes in the growth interface environment have been in-
troduced in two separate ways. In one series of experiments, the main
zone argon purge rate was reduced in steps from previously defined
"standard" conditions to zero. In a second set of tests, gases such as
CO_2, CO, and CH_4 were deliberately introduced into the growth slot near
the interface. Ribbon appearance and growth condition changes which re-
sulted from the introduction of the latter gas species were qualitatively
similar to those obtained with reductions in the main zone argon purge

rate. In all cases, a range of ambient conditions could be found for which ribbon surface film appeared and a marked decrease occurred in the density of visible die-top SiC particle growth and pick-up on the ribbon surface. Associated with a light film cover in many cases was the appearance of significant deviations from the equilibrium defect structure characteristic of EFG ribbon. These were generally in the form of extended regions of what appeared to be large-grained polycrystalline silicon. Meniscus height was observed to be a critical parameter in the ability to achieve growth conditions favorable to continuous film formation and die-top SiC growth suppression. Very low ($\lesssim$ 0.015 cm) meniscus growth in all cases resulted in the appearance of intermittent film cover and a high SiC particle density irrespective of ambient conditions.

As-grown material SPV diffusion length increases above those found with "standard" ambient operating conditions were found to be associated with the appearance of film and SiC particle suppression. They were the most reproducible and largest for ribbon grown with a reduced main zone argon purge rate and with CO_2 introduced into the ambient. The best solar cell efficiencies realized to date (up to 11.5%) have been achieved on the ribbon grown under the reduced main zone purge rate conditions.

B. Crystal Growth

1. Experimental

Studies of the effects of ambient changes in the growth interface environment on quality were extended this quarter to include growth from a cartridge with a cold shoe and deliberate introduction of CO, CO_2, and CH_4. A summary of the experimental data is presented in Table I. In runs 18-155 to 18-169, the main zone purge rate was the chief variable investigated. Runs 18-161, -162, -163, -164, and -166 utilized a cartridge with a cold shoe; the others were made with a separate cartridge without a cold shoe for the purpose of continuing the monitoring of baseline conditions at various main zone purge rate levels. An additional control over the furnace ambient was introduced in run 18-159 by the use of a linear cooling plate modified to provide gas inlets ("gas jets") to the neighborhood of the growth interface. This gas jet configuration was utilized in runs 18-170 to 18-176 to bring CO, CO_2, and CH_4 to the growth interface. Run 18-160 was a special run with an undoped charge consisting of high purity float zone-grown silicon. Run 18-164 was also an undoped run, but with the regular charge material and the cold shoe system.

Table I. Run and Ribbon Data for JPL No. 1. All Runs Used
a Cartridge Without a Cold Shoe, Except as Noted.

Run No.	Speed Range (cm/min)	Length (m)	Comments
18-155	1.6 - 1.8	3.8	Rebuilt cartridge. Reasonable growth condition. Variable purge rate.
18-156	1.8 - 2.4	3.8	Experimentation with purge rates. Reasonable growth conditions.
18-157	1.9 - 2.2	1.4	Poor growth conditions. Growth limited by broken afterheater. Variable purge rate.
18-158	1.8 - 2.1	1.6	Poor growth conditions. Narrow ribbon growth only. Variable purge rate.
18-159	1.8 - 2.1	4.9	First test of interface gas jet flow configuration. Overnight furnace operation.
18-160	1.9 - 2.0	4.0	Undoped float-zoned silicon used for charge. Variable purge rate. Growth conditions below average with frequent freezes.
18-161	2.7 - 3.6	3.5	First run with stretched version of cold shoes. Reasonable growth conditions. Thick ribbon (~0.040 cm).
18-162	3.0 - 3.4	5.8	Second run with cold shoes. Reasonable growth conditions. Thinner ribbon (≤ 0.030 cm).
18-163	3.0 - 3.9	8.9	Third run with cold shoes. Examination of combination of purge rate and meniscus height on film formation. Overnight furnace operation.
18-164	3.2 - 3.5	6.0	Cold shoe run with undoped melt.
18-165	1.8 - 2.0	3.1	Return to baseline growth with rebuilt cartridge, without cold shoe, used in run 18-160. Testing of gas jets on both sides of growth slot.
18-166	1.9 - 3.2	4.4	Fifth run with cold shoes. Investigation of the effect of speed on film formation.

Table I Continued.

Run No.	Speed Range (cm/min)	Length (m)	Comments
18-167	1.8 - 2.0	5.3	Continuation of baseline growth without cold shoes. Further testing of gas jet effect on film formation.
18-168	1.8 - 1.9	2.2	Continuation of baseline runs without cold shoes. Growth limited by water leak external to furnace.
18-169	1.7 - 2.0	3.9	Continuation of baseline run without cold shoes. Testing of gas jets in growth slot.
18-170	2.0 - 2.1	2.8	First experimentation with deliberately introduced CO_2 in growth slot.
18-171	1.6 - 1.8	5.0	Repeat of run 18-170.
18-172	1.6 - 2.0	3.4	Repeat of run 18-170.
18-173	2.0 - 2.1	3.5	First experimentation with deliberately introduced CO in growth slot.
18-174	2.0 - 2.1		Repeat of run 18-173.
18-175	2.0 - 2.1	1.2	First experimentation with deliberately introduced CH_4 in growth slot. Poor growth conditions due to excessive levels of CH_4.
18-176	2.0 - 2.1	4.5	Repeat of run 18-175 at lower CH_4 concentrations.

Several different die designs were used throughout these runs. The basic design was that for the central channel die described in an earlier report.[3] All dies were displaced, either 0.008 cm or 0.012 cm, and had channel widths of between 0.75 cm and 5 cm. Reproducible changes in solar cell properties due to die design variations have not been identified for the runs reported here on the basis of the characterization completed to date. Die design will thus not be considered a variable in the present discussion of the effects of ambient composition on ribbon properties presented below.

The growth system utilizing all graphite main zone insulation, graphite die-top shield and no cold shoes had been employed in the first phase of the ambient study, which examined the effect of main zone purge rate variations on material quality. A means to control backstreaming of air into the growth slot was introduced at this time in the form of a pressurized plenum chamber, or gas "lock," surrounding the ribbon at its exit from the cartridge.[2] This allowed growth stability to be retained at very low purge rates, where air backstreaming otherwise would have caused intolerable disruptions of growth.

The deliberate introduction of a gas species of known concentration into the growth slot was accomplished by use of two gas jets in the manner shown in Fig. 1. One hole drilled in each linear cooling plate at 60° to the vertical exits into the growth slot at a point about 2 cm above the die top. This arrangement allowed manipulation of the interface ambient composition independently of that in the main zone.

A summary of the experimental results is given below with a discussion of the effects observed with main zone purge rate changes in cartridges with and without a cold shoe, and with introduction of CO_2, CO, and CH_4 in the growth interface region.

a. Main Zone Purge Rate Variation Experiments

As described in a previous report,[2] the responses of the growth system to decreases in the main zone argon purge rate generally were reproducible in the experiments carried out in runs 18-143 to 18-150. Decreases in SiC particle growth on the die top and film appearance on the ribbon surface have been attributed to processes associated with increased levels of CO within the furnace. This gas is expected to be the dominant contaminating species inside the furnace under these conditions because of the large surface area of hot graphite parts. These
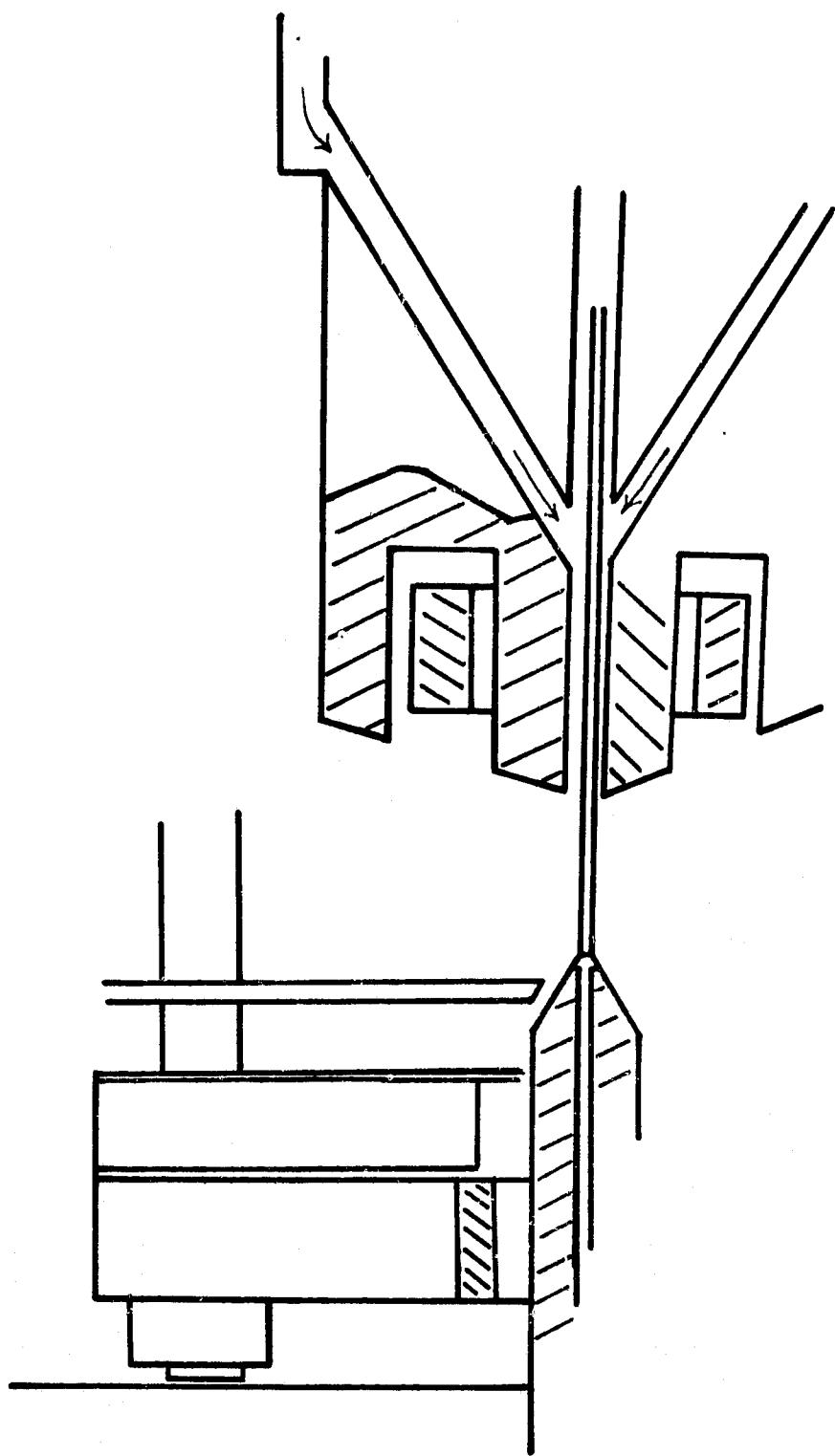
Fig. 1.   Gas jet configuration used in ambient
experiments described in text.

would oxidize rapidly in the presence of other gases, such as CO_2, H_2O, or O_2, to form CO. The CO concentration thus should rise at decreased purge rates as a result of a reduced level of dilution of resident furnace gases (i.e., those originating from outgassing of adsorbed species such as those listed above) and from increased backstreaming of air. If the CO were to affect the balance of carbon (and oxygen) in the melt, processes responsible for formation of SiC particles at the die top would also be affected.

The ribbon surface film has been shown, by means of several "quenching" experiments, to originate mainly through interaction of the furnace ambient and the solid ribbon surface above the interface. In these experiments, growth was abruptly terminated by pulling the ribbon out of the furnace at a rate of about 50 cm/min by suddenly increasing the stroke puller speed from the normal growth speed. At the fast speed, the last-to-freeze section of ribbon is pulled through the highest temperature region of the furnace (above about $1000^{\circ}C$) in approximately five seconds. Ribbon removed from the furnace in this fashion has shown clear demarcation lines between heavy and light film regions, with the boundary location a function of the CO concentration in the furnace.* At the lowest levels for which a light film cover is visible (CO $\lesssim$ 50 ppm), the demarcation line occurs as much as 1 cm above the last-to-freeze part of the ribbon. Under very heavy film conditions (CO $\gtrsim$ 500 ppm) the demarcation line is located very close to the ribbon termination, of the order of 0.1 cm or less. The film has been identified as consisting primarily of SiC with some SiO_x.[2] It also exhibits many of the characteristics described by Yang and Schwuttke[4] for dendritic and epitaxially grown SiC.

An additional manifestation of growth at reduced main zone purge rates has been the presence of a film on the residual bulk melt surface at the completion of a run. It is not known whether this film is formed while the growth system is at operating temperature or during the cooling cycle. The relationship between the composition of the gases in contact with the bulk melt and that at the growth interface is not known. However, it is most probable that the dominant ambient species above the bulk melt at reduced purge rates is also CO, although not necessarily at

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*The CO concentration levels are measured with a Matheson/Kitagawa "length of stain" detector tube.

the same concentration levels as near the interface, and that the ambient-liquid silicon interaction takes place via similar processes in both areas.

Considerable difficulty was experienced in reproducing a given ambient state (as judged by visible film intensity) through main zone purge rate variations in the course of the runs from 18-152 to 18-160. A possible cause of these difficulties, a cartridge water leak, was discovered and fixed after run 18-154. However, even though the cartridge was rebuilt for run 18-155, higher than usual CO levels in the furnace (again, as judged by film intensity at a given purge rate) persisted. Additional possible sources of unwanted gases during this time were a period of particularly humid weather, and the chance that some water had remained behind in the furnace even after the water leak was repaired. These observations suggest that the main zone purge rate is but one of a number of factors to be considered in attempting to achieve controlled ambient conditions during growth of ribbon.

b. Ambient Effects with Cold Shoes

Growth system behavior in a cartridge with a cold shoe was studied over the same range of main zone purge rates that was used in the experiments described in the paragraph above. A growth speed range of 1.8 to 4 cm/min was chosen to overlap, at its lower end, speeds typical for growth without the cold shoes. Decreases in the main zone purge rate were accompanied by increases in the surface film intensity, to qualitatively reproduce the results found without the cold shoe. At the same time, growth conditions for which continuous film cover and die-top SiC suppression could be achieved were more difficult to realize in growth with the cold shoe. Most obviously, film growth at the lower purge rates was very frequently intermittent, more often so on the low meniscus side. This tended to emphasize an asymmetry in the surface film appearance with respect to the two ribbon faces seen only infrequently in growth without the cold shoe. When growth conditions and ribbon edge stability would permit, growth with a higher meniscus usually resulted in a more continuous film being formed. In the case of very low meniscus growth, the ribbon surface growing from above the nondisplaced die side characteristically alternated between a high SiC particle density and patches of film. The onset or interruption of film-covered surface on this ribbon face appeared to be associated more with specific growth conditions (i.e., the meniscus height) than with the main zone purge rate magnitude. On the

12

other hand, this was not the case for the film appearing on the ribbon face growing from above the low die-top side. The film occurring there was generally continuous and intensity, as judged visually, was dependent on the main zone purge rate magnitude in much the same way as found for growth without the cold shoe.

c. CO_2, CO, and CH_4 Ambients

Changes in ribbon properties observed with reduced main zone purge rates have suggested that variations in the concentration of contaminating ambient gases, such as CO, exert an important influence on interface melt conditions during growth. To examine this interaction in a more controlled manner, growth was carried out while a specific gas of known concentration was introduced into the interface environment. The gas jet configuration installed in the cartridge without a cold shoe was used for these experiments (see Fig. 1). The preliminary experiments done to date have consisted of several runs each with one specific gas, with the species chosen to explore a range of possible ambient interactions with the silicon melt.

Carbon dioxide was chosen as representative of an ambient gas which could increase the partial pressure of oxygen through interaction with hot carbon and silicon melt. Ambient conditions in both runs 18-170 and 18-171 were alternated between a standard reference ambient and one with 1% CO_2 in argon flowing through the gas jets. Run 18-172 was carried out with a low level of CO_2 maintained throughout the run.

Carbon monoxide was chosen to contrast CO_2 in decreasing the oxygen availability to the ribbon and melt, while also simulating ambient conditions suspected to arise during growth at reduced main zone purge rates. Methane was chosen to provide another extreme, a reducing ambient. Experiments similar in scope to those for CO_2 were carried out with CO and CH_4 in runs 18-173 to 18-176. Due to the availability of only a 50% mixture of each of the latter in argon, the tank concentrations were diluted to reduce them to levels below 1%.

In overall responses, all three gas species examined produced similar changes in growth conditions and led to film formation on the ribbon. Growth difficulties were experienced with mixer gas concentrations of about 1% and above. These usually were caused by build-up of deposits on the die top. For CO_2 and CO, the deposits appeared to consist of SiO_2 and SiC. The latter appeared to be more dispersed and discrete than that produced during growth from the die top. Carbon "soot" was abundantly

produced at high CH_4 concentrations. Patches of carbon deposits were particularly effective in disrupting the die top thermal balance. Ribbon gilm cover was heavy in this high concentration range, and growth conditions deteriorated very rapidly with continued exposure of the die top to these gases.

The initial attempt to grow with a 1% CO in argon mixture showed that lower CO_2 concentration levels would be required to avoid excessive die top deposits and to maintain acceptable growth conditions. A means to further dilute the mixture exiting from the gas jets was not available at this time. Instead, low flow rates were tried to attempt to reduce the CO_2 levels near the growth interface, and at rates of about 200 cc/min growth conditions were found to be acceptable. An entire run, 18-172, was carried out under these conditions. Film cover was generally continuous, with still moderate to heavy film intensity. The SiC particle density was very low, and comparable to the levels achieved with reduced main zone rates. Occasional larger grain growth was also observed.

A mixer was utilized, starting with run 18-173, to further dilute the 50% CO and CH_4 in argon tank mixtures. Reasonable growth conditions were usually maintained for mixer gas concentrations below about one-half percent. In an intermediate concentration range, from 1000 to 5000 ppm (0.1 to 0.5%), film cover was characterized as moderate to heavy. Although discrete SiC particle growth at the die-top was greatly reduced, die-top deposits were frequently picked up on the ribbon surface in place of the SiC particles. Conditions of light film cover were realized at mixer gas species concentrations of less than about 1000 ppm. These appeared to be comparable to those achieved at reduced main zone purge rates in that the tendency toward large grain growth increased and the SiC particle density was very low.

Inspection of the bulk melt surface after each run in which the gas jets were used showed that the influence of the gas species introduced in this way did not penetrate to the crucible environment. Except in runs where the main zone purge rate decreases were concurrently made, the melt surface remained shiny with no visible film, after run completion.

2. Material Quality Considerations

Characterization of as-grown material and solar cell data for the ribbon grown under different ambient conditions described above are discussed and compared in Section IV. SPV diffusion length increases have been found to accompany the introduction of CO_2, CO, and CH_4 into

the growth slot. The most reproducible increases have occurred for CO_2, the most inconsistent results have been for CH_4. At their best, the SPV increases are comparable to those achieved with reductions in the main zone purge rate. Solar cell performance for ribbon grown in the different ambients has not always been improved commensurately with the higher SPV diffusion lengths. The characterization results, as they relate to the understanding of the ambient influence on the growth conditions and material quality, are discussed below in more detail.

In runs 18-153 to 18-160, efforts were made to reproduce growth conditions at low main zone purge rates, which had resulted in the high diffusion lengths and solar cell efficiencies reported for runs 18-143, -148, and -150.[2] Conditions were generally poor for reasons given above, with frequent freezes. Some ribbon splitting also occurred because of a malfunctioning afterheater. Good as-grown material quality, as indicated by SPV diffusion length averages between 40 and 50 μm, was retained in spite of these difficulties. However, in contrast to the earlier group of runs, improved SPV diffusion lengths were found even in ribbon grown at the higher purge rates in these later runs. For example, the range of flow rates below 4 ℓ/min, for which earlier quality improvement were realized, was found to lead to much heavier film than permissible from the standpoint of maintaining acceptable growth conditions. Going to higher flow rates of up to 20 ℓ/min subsequently did not entirely eliminate the film or lead to SPV diffusion degradation to the lower levels characteristic of "standard" purge rate conditions established in previous runs. An absence of a correlation of SPV values with purge rate magnitude was interpreted as indicating that the primary influence of the purge rate was in setting the composition of the furnace ambient gases, or diluting them, as may be appropriate.

Only a few solar cells were made with the ribbon grown in runs 18-155 to 18-159 because of a shortage of suitable material. The limited results indicate that the cell performance levels expected on the basis of the measured SPV diffusion lengths in the as-grown material were not realized. At present, there is no indication whether this has occurred on account of a change in the growth system or in cell processing.

In runs 18-161 through 18-169, experimentation with the main zone purge rate was continued to compare growth in a cartridge with cold shoes to that without. Film appearance as a result of the purge rate manipulation in the runs with the cold shoes has not been consistently associated with improvements in SPV diffusion lengths of the magnitude observed for

ribbon grown without the cold shoe. The former usually averaged lower
than the latter (see Section IV). Correlations of ribbon growth speed
with SPV diffusion lengths were not found in the range of speeds from
1.8 to 3.9 cm/min covered in run 18-166.[3] In other runs, higher values
of diffusion length were often found in ribbon grown at the top end of
this speed range than obtained in run 18-166 at lower speeds.

The SPV data presented in Table VIII of Section IV shows reproduci-
ble changes in SPV diffusion lengths occur with the introduction of CO_2,
CO, and to a lesser extent, CH_4, into the growth slot. The diffusion
length changes observed reproduce qualitatively the trends already noted
in the experiments with reduced main zone purge rates. In all cases, the
SPV values increase with the introduction of the gas species. Aside from
the demonstrated influence of the ambient species, other factors have to
be recognized as entering into the evaluation of the effects of a specif-
ic ambient change on material properties. These are examined below:

First, baseline levels under "standard" conditions change from run
to run. The reasons for this are not known. The changes observed may
reflect uncertainties in the SPV measurement as well as differences in
system contamination and starting growth conditions, e.g., meniscus
height, which influences the ribbon thickness profile, and also convec-
tive cooling rate changes due to flow rate variations. (For example,
turning on the gas jet with only argon has a demonstrable effect on the
ribbon thickness and meniscus height. The greatest effect is felt at
the ribbon center, which is preferentially cooled by convection as a re-
sult of the central gas jet location.)

Changes in interface thermal conditions are further reflected in
the meniscus height during the time of film build-up on the ribbon sur-
face, as follows an ambient composition flow rate change. Part of this
thermal effect is attributed to a variation in the convective heat re-
moval rate, as noted above. A more significant factor is felt to be the
increase in the ribbon surface emissivity as a result of film formation,
hence altering the heat transfer balance between the ribbon and its en-
vironment. The net result is that a given set of growth conditions,
i.e., meniscus height, ribbon thickness profile and interface shape, is
probably never reporudced at each new ambient condition.

Another variable which may influence the results is the concentra-
tion, at the growth interface, of the gas species introduced via the gas
jets. For the data reported, flow rates were different in the CO_2 ex-
periments from those done with the CO and CH_4 for the reason noted above.

16

Correlations of the species mixer composition and SPV data were not evident for any of the gases (see Section IV) in the course of the preliminary experiments done to date. An important consideration in this respect is that ribbon growth conditions start to deteriorate at the upper end of the concentration range used for all the gas species, and this sets a practical limit with respect to the usefulness of the data obtained.

Other evidence also indicates indirectly that the penetration of a given gas species to the growth interface is not uniform. Ribbon surface film patterns often reflect concentration nonuniformity introduced by deviations of the ribbon from flatness. These patterns appear to vary with the ribbon surface-to-linear cooling plate separation, which affects the local exit gas velocity and consequently alters the gas species' concentration at a given location near the ribbon surface. In addition, gas jet nonuniformity is evident in the appearance of stains along the ribbon center line opposite the gas jet openings when argon alone is exiting. This suggests some residual contamination of the argon by gases such as oxygen or water vapor. However, specific effects on quality and on growth conditions due to this interaction have not been observed, presumably because of the low concentrations of these contaminating gases.

As a final consideration, long term transient effects are also frequently observed to influence growth conditions. These involve contamination and subsequent outgassing of furnace and cartridge components through adsorbed or reacted gas species. One such example was given above in connection with suspected contamination arising from water vapor as the source. The use of CO_2, CO, and CH_4 also has demonstrable effects over a longer term through the formation of reaction products in the form of deposits retained on furnace and cartridge components from run to run. These deposits are thought to exert considerable influence on the partial pressures of all the residual furnace ambient gases, such as CO, SiO, CO_2, and O_2, which are therefore not constant from run to run.

In summary, first order effects on growth conditions and material quality have been clearly demonstrated in the experiments at reduced main zone purge rates and through use of CO_2, CO, and CH_4 ambients. Although the establishment of quantitative trends in quality responses will have to await more extensive and detailed characterization, the significance of even small changes in ambient conditions cannot be minimized.

17

If a given change has an immediate effect on the composition of such impurities as carbon and/or oxygen in the melt (meniscus as well as bulk), as is believed, then it is extremely important to establish a means of control over ambient species that can be used to take advantage of the benefits to be gained from processes which promote SiC particle suppression and large grain growth.

Possible mechanisms for the ambient gas-silicon melt and ribbon interaction were briefly discussed in a previous report.[2] The present level of understanding of these processes is still based mainly on only visible inspection of the ribbon film condition and observation of the die top during growth. Characterization of the material with respect to film composition and bulk properties is in progress. This will allow a better evaluation of the differences in ribbon properties which arise as a consequence of ambient changes.

3. Future Work

The present growth system design imposes severe limitations on the types of experiments that can be carried out with ambient gases and the extent of the control that can be exercised on its composition. Considerable effort will be devoted to attempting to improve this situation in the near future. Changes are planned that will reduce air leaks into the system still further, and allow sampling, as well as introduction of, ambient species in regions of the growth system other than via the gas jets. In the meantime, additional experiments with selected ambient gases and reduced main zone purge rates are being planned to better delineate the range of concentrations of gas species that give the most reproducible results in the case of the phenomena observed.

III. MULTIPLE FURNACE 3A by B.H. Mackintosh

A. Review of Multiple 5 cm Ribbon Development, October 1978
    Through May 1979

Within the past year, the EFG ribbon technology reached an important
milestone in the demonstration of high-throughput operation of the 5 x 5
cm multiple furnace, which produced silicon sheet usable for solar cells
of moderately high efficiency. Approximately one year ago, several im-
portant elements of this technology were emerging from experimental and
design work on this system. The stability and repeatability of operation
of the 5 cm growth cartridge was being developed to a point where several
hours of full-width growth at 3.5 cm/min could be expected each time the
machine was run. The ability to perform relatively long runs under con-
trolled conditions permitted a meaningful evaluation to be made of the
electronic properties of this ribbon. Displaced-tip dies were proving to
be a useful means of improving the photovoltaic quality of this ribbon.

In the first quarter of 1979, a new multiple cartridge hot zone was
installed and developed for satisfactory operation. Its design embodied
many improvements over the previous one in reliability, cleanliness, and
ease of operation. Also in this quarter, the continuous silicon feeding
system which was first used in the multiple growth demonstration runs of
January 1978, was further evaluated and refined. This evaluation in-
cluded, for the first time, operation of the furnace in fully clean mode
with continuous silicon feeding, and measurement of electronic properties
of the resulting ribbon. A conclusion drawn from these measurements was
that solar cell material grown from replenished melts was not signifi-
cantly different from that produced in non-replenished runs.

These elements of technology development were brought together in
the second quarter of 1979 in two highly successful five-ribbon demon-
stration runs, whose outcome surpassed the throughput goals and very

19

nearly attained the solar cell performance goals of the 1978 contract year. The outcomes of these runs are described in detail in the Second Quarterly Report;[4] tables depicting the throughput performance of the system and solar cell performance of material from the last of these runs are reproduced from that report in Appendix 4.

B. Development of 10 cm Ribbon Growth

1. Design of 10 cm Cartridge

Late in 1978, the design of a growth cartridge for 10 cm ribbon, to eventually replace the existing 5 cm and 7.5 cm cartridges, was undertaken. Although the basic configuration of the latter two units was retained, several detail refinements were made to improve reliability and ease of operation. The most significant change designed into the new cartridge was a smaller and more nearly constant temperature gradient in the linear cooling region. The reasons for, and implications of, this change are discussed below.

The first unit of the new 10 cm cartridge and associated equipment were ready for use in Furnace 3A, when the multiple 5 cm demonstration runs were completed in late May, and are shown in Figs. 2, 3, and 4. More details are available in earlier reports.[3,5]

2. Goals for 10 cm Multiple Ribbon Growth

Under the current phase of this project, the equipment and techniques for 10 cm ribbon are being developed toward demonstration of multiple growth by the end of 1979. Furnace 3A will by then be outfitted with three 10 cm growth stations, the number permitted by the length of the existing chamber. The emphasis in this developmental phase through the end of 1979 is on the mechanical or throughput aspects of the process, with no specifications having been made for the photovoltaic performance of ribbon grown in this multiple mode. The goals are a minimum of two hours simultaneous growth at 10 cm width x 3.5 cm/min.

3. Development of 10 cm Ribbon Growth, May 1979 through September 1979

Table II summarizes all 10 cm ribbon runs performed to date in Furnace 3A. Further description of the development process is as follows:

SECTION N-N   SECTION M-M
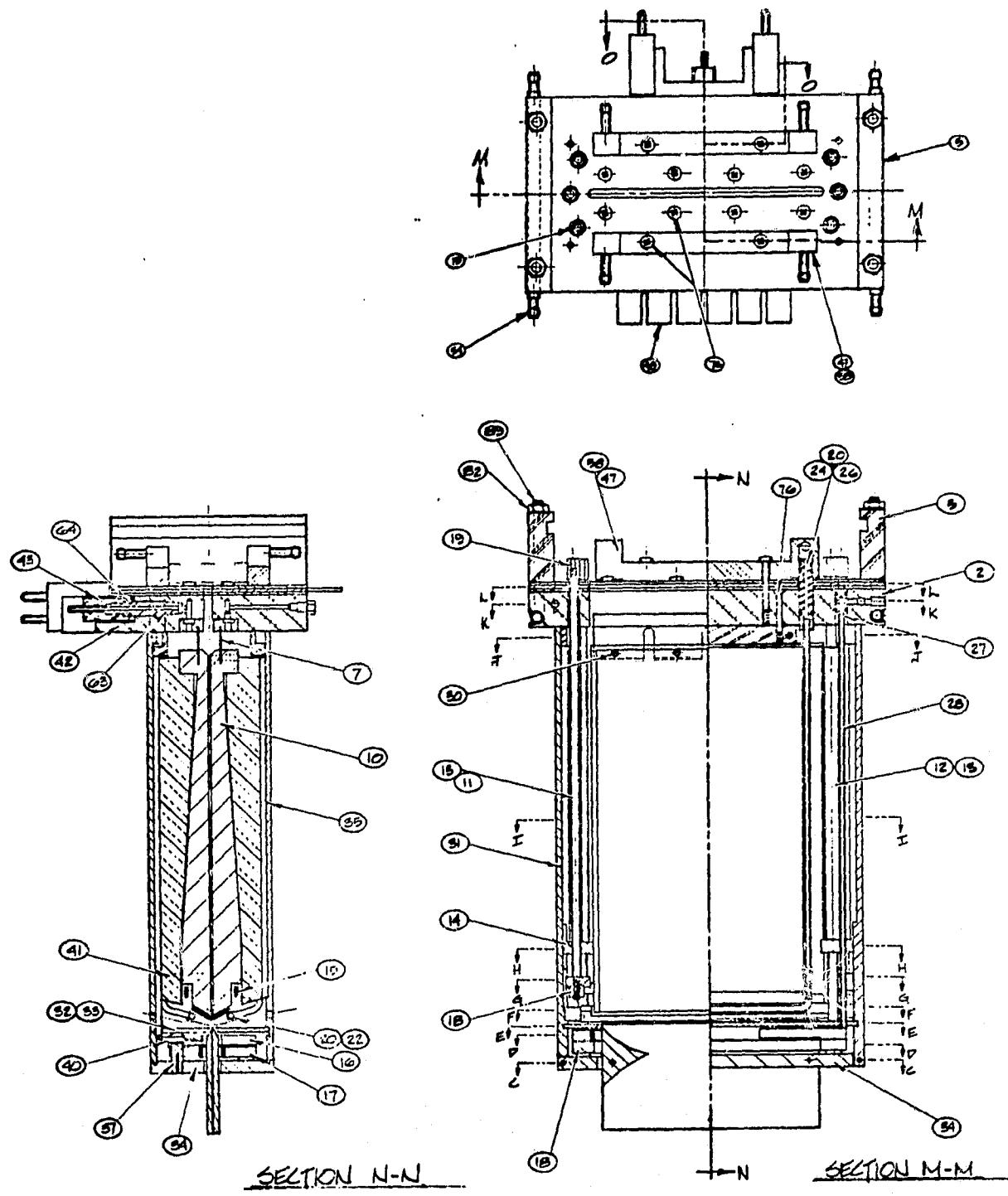
Fig. 2.   10 cm ribbon cartridge.

21
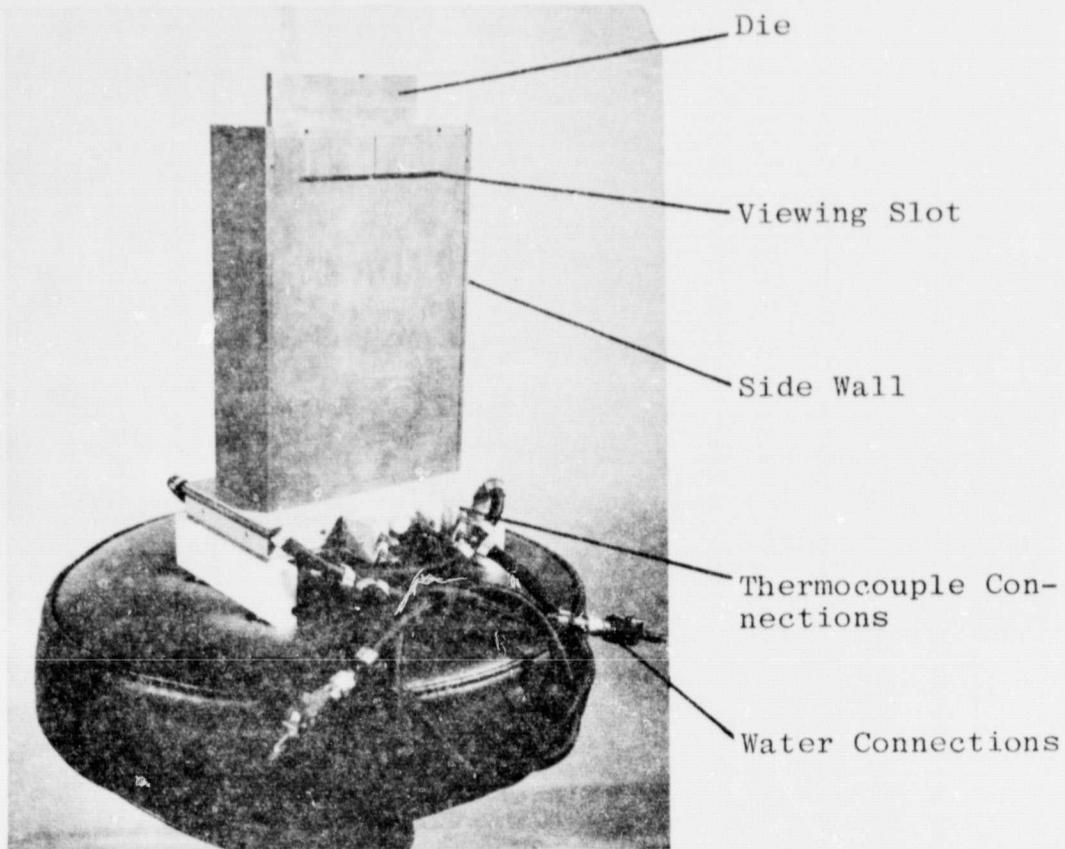
Fig. 3.   10 cm ribbon cartridge, complete.

Die

Die Heaters

Afterheater
Element

Linear Cooling
Region

Heater Current
Connections

Mounting to
Puller
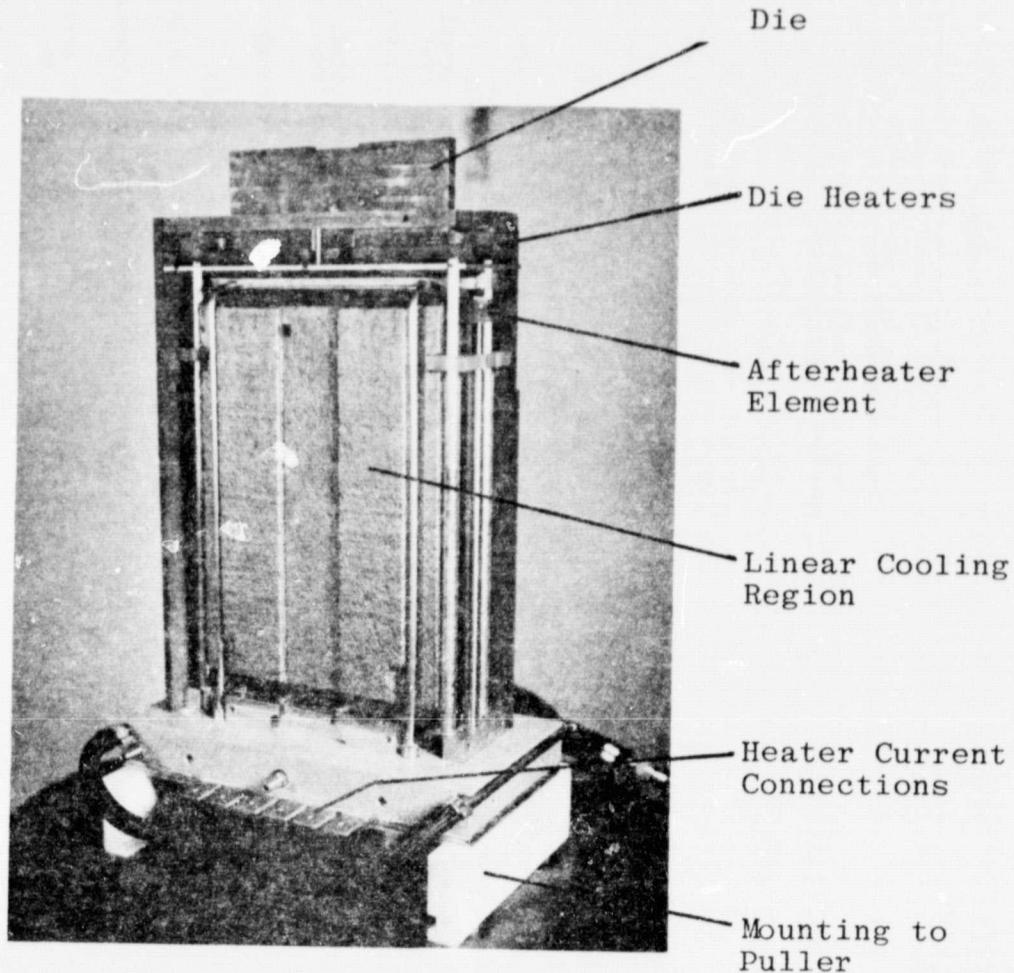
Fig. 4. 10 cm cartridge with side wall and cover removed.

Table II.   10 cm Ribbon Growth Runs, Furnace 3A, June Through September, 1979.

Run No.	Die S = Slot Width (cm)	D = Displacement (cm)	B = Bulbs*	C = Capillary Type**	Cold Shoes H = Height (cm)	T = Face Thickness (cm)	End Heater Length (cm)	Replenished	Qty. Full Width (m)	Stability	Comments
188	.051	0	0	D	.094	.24	2.8	No	0	Poor	First run with 10 cm cartridge – maximum width attained 7 cm.
189	.051	0	0	D	.094	"	"	"	0	Fair	Relatively cold die center -- ribbon couldn't be spread beyond 7.5 cm.
190	.051	0	0	D	.094	"	"	"	0	Fair	Similar to run 189. Terminated due to broken ribbon.
191	.051	0	0	D	.150	"	"	"	0.2	Fair	Changed end heater thickness to make extreme die ends hotter. Run ended while growing 10+ cm wide due to melt depletion.
192	.051	0	0	D	.115	"	"	"	0	Fair	Cold die center; run devoted to growing seed material.
193	.051	0	0	D	.115	"	"	"	3.5	Good	Thinned center of face heater bars; improved die temperature profile.
194	.051	0	0	D	.130	"	"	"	3.1	Good	Growth rate over 3.6 cm/min. Ribbon stressed and breaking in puller.
195	.038	.013	0	D	"	"	"	Yes	3.3	Fair	Heavy SiC despite die displacement. Displacement and thinner slot made growth less stable. Rate up to 4.2 cm/min.
196	.038	.013	N	SC	"	"	"	"	1.6	Fair	Mechanical guidance problems (ripples) causing freezes.
197	.038	.015	0	D	"	"	"	"	3.3	Good	Cold shoes straightened and centered. Good growth with lower SiC than previous two runs.
198	.038	.015	0	SC	"	"	"	"	8.5	Good	Two two-hour continuous growth periods. Average rate 3.48 cm/min.
199	.038	.015	"	SC	"	"	3.5	"	3.5	Good	Two-hour continuous growth period.
200	.038	.018	B	SC	"	"	2.8	"	6.4	Good	First test of bulbous-ended die. Heavy SiC, both faces of ribbon.
201	.038	.018	B	SC	"	"	"	"	1.8	Good	Demonstrated full-width seeding; measured [CO] in cartridge.
202	.038	.018	B	SC	"	"	"	"	0	-	Replaced moly did top shield with graphite. Silicon bridged from die to shield.
203	.038	.018	B	SC	"	"	"	"	0	-	Seed broke in cartridge; crucible failed causing silicon flood.

*Bulb (end stabilizing feature): 0 = none, N = notches, B = bulbs.
**Capillary type: D = five drilled holes in center, SC = saw cut capillary.

In May, the basic mechanical, thermal, and electrical performance of the cartridge was evaluated prior to attempting growth. In June, the process was undertaken of modifying the face and end heaters to obtain a suitably-shaped isotherm across the width of the die which would permit controllable spreading and full-width ribbon growth. A die with a relatively wide, featureless top (no bulbs or displacement) was used at this stage to facilitate growth under non-ideal thermal conditions.

Once satisfactory full-width growth had been achieved with this initial die type, four changes were made during July to advance the 10 cm growth art toward the state which the 5 cm ribbon technique had attained when it was discontinued. The changes were: (a) installation of the continuous melt feeder, (b) substitution of dies having smaller tip width, (c) addition of die tip displacement, and (d) assembly of the cartridge using all purified graphite parts.

The continuous melt replenishment unit was seen not to have a serious effect on performance of the cartridge, and has been used in all runs subsequent to No. 16-195. It has been responsible for a slight lateral temperature imbalance, correctible by end heater settings, in the adjacent cartridge.

Irregularities in the thickness profile of ribbon grown from the thinner die suggested a further refinement of the face heater/end heater combination.

Good stability was exhibited in the three runs made in August. On three occasions, full-width growth proceeded for two hour periods without freezing. These steady-state growth conditions, and the efforts made to assemble the furnace in a clean condition, permitted the first meaningful measurements to be made of the electronic properties of 10 cm ribbon. The SPV data for runs 16-197 through 16-199 appear in Table X of Section IV.

The displaced tip dies used in August were not effective in growing ribbon with one surface completely free of silicon carbide particles. The difference between the two ribbon surfaces, although evident throughout these runs, was most distinct in run 16-198, in which several meters were grown with "moderate" silicon carbide particle density (3 to 10 per 50 cm^2 cell blank). These dies lacked the end-stabilizing bulbs which were a feature of the dies used in all recent 5 cm growth work. Besides their primary function of stabilizing ribbon against temperature fluctuations, these end bulbs can positively impact ribbon quality by permitting the growth meniscus to be raised to a higher level across the

rest of the die. A certain minimum value of meniscus height is one of the conditions required for the displaced-tip dies to function as intended, i.e., to cause virtually all of the carbon leaving solution at the interface to grow into silicon carbide crystallites on the high die tip. Growth with a higher meniscus also yields thinner ribbon from a given die tip width.

Growth experiments with bulbous-ended dies began in the runs of September. In the first two of these runs, full-width growth was maintained for several meters. Ribbon from this first run served as a seed in the second to demonstrate initiation of growth without loss of width. To be able to do so is extremely important when an operator must monitor and control multiple ribbons. These two runs which were successful in yielding ribbon were, however, only preliminary in the process of defining the optimum die/heater combination and developing growth technique. The heating element combination in place during these runs did not permit full advantage to be taken of the bulbs for raising the central-region meniscus to effect quality improvements as discussed above. (The subject of die heater optimization is further discussed below.)

Experiments with heater/die combinations were interrupted by a cartridge component change made prior to the third run. Specifically, the molybdenum die-top radiation shield was replaced with one made of graphite, in order to reduce the possibility of contamination with Mo and its impurities. Neither of the subsequent two runs, the last in the reporting period, produced any ribbon, due to silicon floods.

4. Important Differences Between 5 cm and 10 cm Systems

The following paragraphs discuss the most fundamental differences between the 5 cm and 10 cm cartridges in terms of operating technique, developmental emphasis, and ribbon mechanical properties.

a. Viewing of Die

The scale-up in ribbon width results in a significant difference between the two systems in operator technique. An optical magnification, which permits the operator using a conventional microscope to discern details of the meniscus height, limits the width of the field of view to about 5 cm. The inability to see both the ends of the 10 cm die at once makes the procedure of initiating growth much more difficult than was the case with 5 cm ribbon. An anamorphic optical system as is

used on Furnace 17 will be extremely useful to reduce the level of skill demanded of the operator for this procedure. These optical systems will be installed in early 1980, in conjunction with the work on automatic controls planned for this system.

b. Spreading of Ribbon; End-to-Center Balance

In the case of the 5 cm cartridge, a pair of end heaters surrounding approximately 1 cm of each end of the die gave good control of ribbon edges in a spreading mode, and satisfactory thickness profiles in full-width growth of 5 cm ribbon. In the case of 10 cm wide ribbon, the same proportion of end heater coverage to die width (i.e., 2 cm end heaters) also gives optimum control over ribbon spreading when full-width seeds are not available, or when poor control during the starting transient results in loss of width. In these two instances, it is necessary to effect left-right and end-center thermal balance on ribbon edges up to 2 cm from the die end. This broad region of influence, however, is a disadvantage in full-width growth. Here, one should be able to heat up a central region of the die, at least 9 cm wide, to raise the meniscus and thin the ribbon, controlling the isotherm shape only in the outermost few millimeters with end heaters. When this is attempted with the current face heater/end heater combination, only the central 5 to 6 cm of ribbon is thinned. This thickness profile makes re-seeding after freezes more difficult, and is not acceptable from a solar cell fabrication standpoint.

c. Ribbon Flatness and Stress

Three changes were made in the 10 cm cartridge relative to the earlier versions to obtain flatter ribbon with acceptably low stress.

(i) The temperature profile of the linear cooling region was modified for a smaller temperature gradient over the same length and hence a higher ending temperature. With this smaller gradient, the ribbon spends a longer time in a region where its temperature is sufficiently high that stresses generated by the transition from the initial high gradient to the low cooling gradient can be relieved.

(ii) The afterheater element was placed nearer the low end of the linear cooling plates, and adjacent to their outer wall rather than in a slot cut in the middle of their thickness dimension.

The gas distribution block which interrupted the thermal conduction cross section of the linear cooling plates just above this point in the 5 cm cartridge was eliminated. As a result, the surface temperature decrease of these plates along the growth direction is more nearly linear. Figure 5 shows representative profiles of the 5 cm and 10 cm cartridge linear cooling regions.

(iii) Better guiding surfaces were provided for the ribbon to minimize its deviations from perfect alignment with the die and to constrain it from relaxing stresses in the plane by buckling to large amplitudes. Although the buckling and stress characteristics of this cartridge have not been closely studied, the following observations have been made.

Flatness: The patterns of clearly periodic edge buckling or center buckling often present in 7.5 cm and 5 cm ribbon growth have not been observed in 10 cm ribbon. Ripples which are approximately "in phase" across the ribbon width, and quasi-periodic over limited ribbon lengths, are seen. These are due to "guidance" disturbances, and are limited in amplitude (as all deviations must be) by the slot through which the ribbon passes. Although the flatness of typical segments grown from this system is already compatible with Mobil Tyco solar cell making procedures, some further optimization of the guiding surfaces and other factors affecting flatness seems possible.

Stress: Ten cm wide ribbon has not shown the tendency to split straight up the middle, which was a sign of excessive residual stresses in 5 cm and 7.5 cm ribbons. The typical breakage pattern has instead been for a more or less rectangular corner, several centimeters on a side, to break off the end of a segment.

It has also been difficult to scribe-and-break the 10 cm material along lines perpendicular to the growth direction, as the break often departs from the scribed line somewhere across the width. The spontaneous breakage of seed ribbons inside the cartridge has been an inconvenience, as discussed below. Part of this overall breakage problem has been due to the lack of proper scribing fixtures and less-than-careful handling.
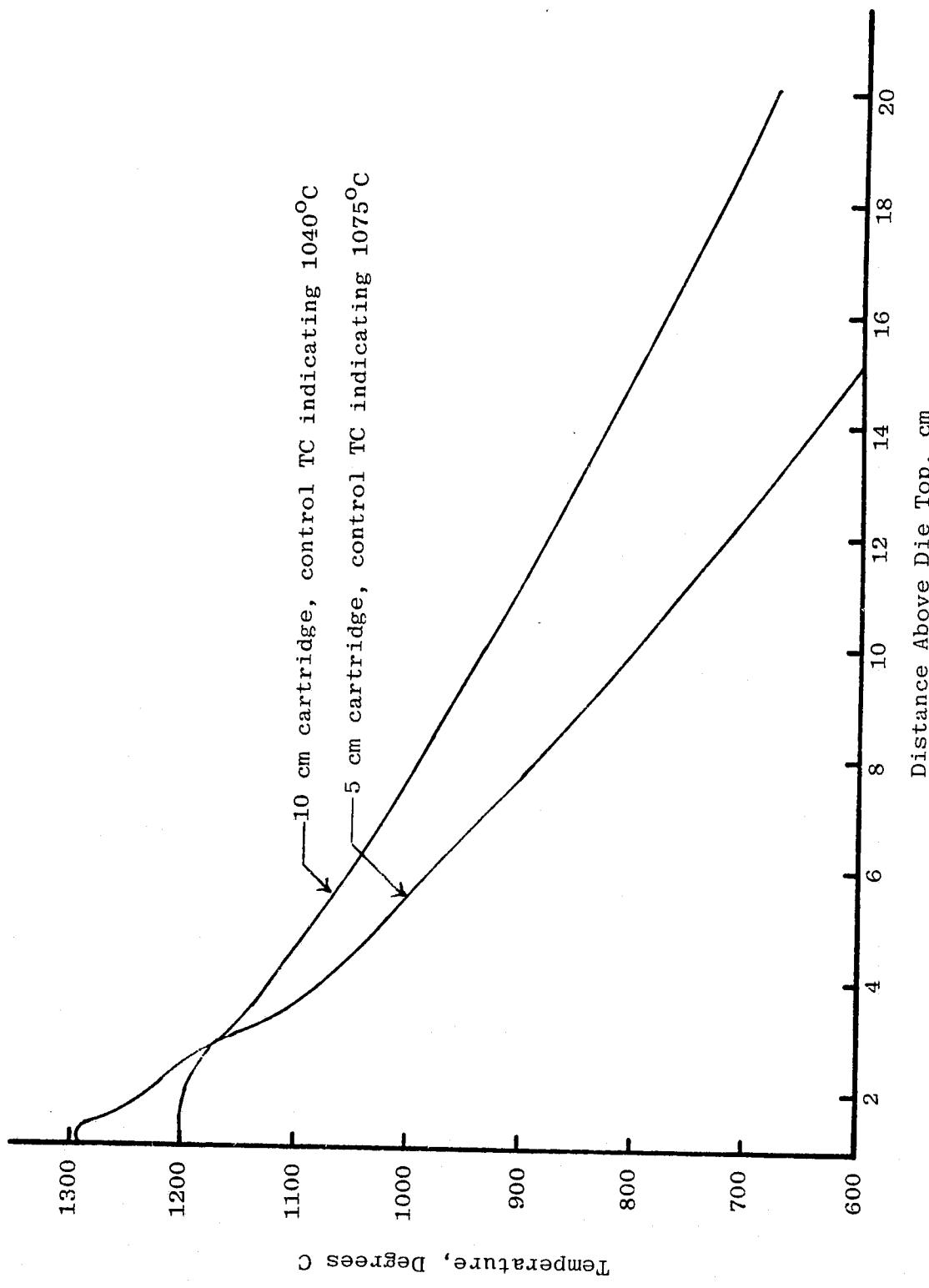
Fig. 5. Temperature profiles of linear cooling regions of 5 cm and 10 cm cartridges, taken with conventional wire thermocouples.

One measurement of stress by the multiple-finger method* was made on 10 cm ribbon. It is represented by Fig. 6, which includes similar measurements on 7.5 cm ribbon for comparison. Due to different after-heater designs and thermocouple placements, the temperatures given don't necessarily indicate comparable peak afterheater temperatures. However, the similarity between the two cases in stress distribution and peak stress level is obvious.

An implication of having a similar peak stress in material farther from the ribbon's center line is, no doubt, a higher tensile stress across the center line near the cut end of a piece. When a split occurs as a result of this stress, the bodies on the two sides of the crack are so stiff that they deflect little and do not produce a visible gap from the typical length of split observed to date. Also, the pieces apparently are still sufficiently wide to have large stresses within themselves, which can be relaxed by having the crack follow grain boundaries or other lines of weakness not necessarily on the ribbon center line. A systematic study of stress vs. afterheater setting and horizontal gradient remains to be carried out on this system. The extent to which stresses are a problem of practical importance remains to be seen.

5. Miscellaneous Problems Experienced in 10 cm Growth

Development of the apparatus and technique for 10 cm ribbon growth has been hindered by several problems not explicitly discussed above. These difficulties are not considered to have a serious long-term impact; their solutions will soon be, or are, currently being implemented.

a. Die Capillary Design

Although the die tip configuration has been of principal importance in the developmental runs performed to date, the design of the capillary channel for feeding silicon up the die has also been varied. None of the three capillary types used has been satisfactory in all respects. The first two types were suspected of restricting the flow of silicon to the die ends because of intermittent poor growth stability which had no other apparent cause. The third type performed

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*This stress evaluation technique is described in the First Quarterly Report of 1979.
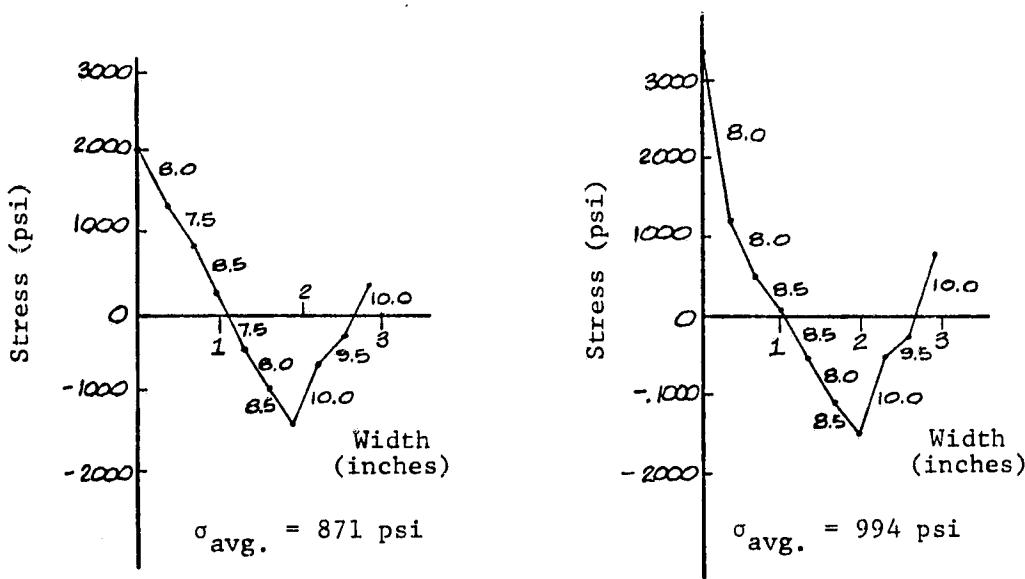
Fig. 6a. 7.5 cm ribbon stress measurements – afterheater
temperature – 1130°C (reproduced from First
Quarterly Report).
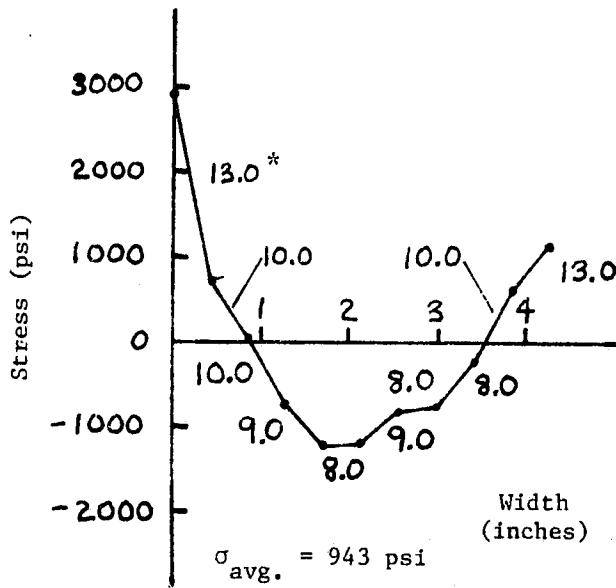
*Figures adjacent to graph segments indicate
ribbon thickness in mils.

Fig. 6b. 10 cm ribbon stress measurements – afterheater
temperature – 1035°C.

well in some instances but in others filled improperly, forming a large gas bubble.

This is principally a problem of manufacturing. All these dies are of a one-piece design; this experience simply shows that the types of holes and slots which can be machined to the required depth without undue difficulty are not properly shaped to serve as silicon capillaries. We are, therefore, reverting to the two-piece die configuration used in 5 cm and 7.5 cm growth which permits proper capillary passages to be machined.

b. Seed Material - Availability and Breakage

The choice of the ideal die heater combination and development of techniques of well-controlled full-width growth would be greatly facilitated by having a supply of good seed ribbons. Such seed material would be straight, perfectly flat, of uniform thickness across the width, able to pass through the puller without hindrance, stress-free, and strong to survive the thermal stresses induced by the cartridge without breaking. Seed material having these qualities has not generally been available during this period. It has generally been possible to grow 10 cm wide ribbon only by spreading from narrower pieces. Much of the resulting wide material has been nonuniform in thickness across the width, and hence unsuitable for seeding, as discussed in 4(b) above.

Finally, ribbon pieces acceptable for seeding purposes have often been broken at three locations in the overall system, as follows:

(i) The process of cutting ribbon perpendicular to the growth direction has been difficult, as described in 4(c) above.

(ii) Several seed ribbons have broken as they entered the linear cooling plate region of the cartridge, probably due to a combination of thermal stress, edge or surface damage, and mechanical stress applied by the puller. The abrupt transition from room temperature to the linear cooling plates at 600°C, combined with the greater width of the ribbon, impose a higher thermal stress at this point than do the other cartridges. However, most seed ribbons survive this stress going in, and all newly-grown ribbon apparently survives it coming out. Hence, this problem can be re-stated in terms of this cartridge having a lower tolerance than others for mechanically damaged ribbon. Cracks and nicks which concentrate stresses are more likely to propagate. Regardless of the findings of future residual stress studies, part of the solu-

tion to this problem lies in carefully inspecting seed ribbons.

A new belt puller is being designed which applies gripping force to the ribbon symmetrically from the two sides and thereby will impose less mechanical stress in the area just above the cartridge than in the puller currently in use.

(iii) Seeds have also frequently split up from the end when inserted to just above the die, i.e., when exposed to the temperature gradient between the cold shoes and linear cooling plates. Until it is attached to the die top, the ribbon end near the cold shoes is colder than the portion of ribbon above it in the afterheater, placing it under tensile stress. (When the ribbon contacts the die, this stress is reduced as the reverse gradient disappears, due to the contribution of heat by the die.) Once again, seed-ribbon breakage at this location can be minimized by careful selection and handling of the material used for this purpose.

6. Future Work

In the coming quarter, work will be directed primarily toward optimization of die and heater configurations for high-meniscus full-width growth with good stability. The additional two cartridges and subsystems will be built and multiple growth runs will be performed before the end of the year.

IV. CELL AND MATERIALS CHARACTERIZATION

A. Cell Characterization (C.T. Ho)

1. Overview

In the past year, several advancements have been made in terms of measurement technique and solar cell fabrication. In the former case, we have redesigned the Schottky barrier geometric pattern in order to address the problem of the inhomogeneous nature of the grown ribbons. By reducing the diode size and arranging them in an array, we found that the SPV measurement results produced more reproducible and reliable data than before. The measurement also yields the information in regard to the distribution of diffusion length across the ribbon width. We have completed the development of a superlinear photovoltaic response measurement technique to study the enhancement effect in the ribbon solar cells. It has been proven to be a useful tool to investigate the effect of fabrication processes on the ribbons grown from various ambient conditions.

In the solar cell fabrication area, efforts have been made to formulate and consolidate a program ensuring the continual solar cell evaluation on resistance-heater grown ribbons. The standard gas phase (PH_3) diffusion and doped oxide (CVD) diffusion have been critically compared. Results indicated that the choice of diffusion process should largely depend on the ribbon growth methods. Attempts have also been made to optimize the solar cell fabrication procedures in order to achieve a 12% conversion efficiency on a minimum 2 x 2 cm^2 area.

2. Introduction

Work in this quarter was concentrated on the routine solar cell fabrication and evaluation for the materials grown from the various growth experiments performed in growth system No. 1. The experiments

included growth with reduced main zone gas as well as growth with various gases mixing with the main zone gas. In both cases, there was a noticeable increase in the occurrence of crystalline grains in the ribbon. In run 18-150 (a reduced ambient gas experiment), the diffusion length in the large grain portions has been measured as high as 57 μm, and conversion efficiencies as high as 11.5% were achieved for solar cells in a batch of large area (55 cm^2) devices.

However, preliminary cell evaluation results of the gas mixing growth experiment apparently indicate that the gas mixture does not have an equally strong effect on the ribbon photovoltaic properties after processing into solar cells. It is speculated that, in this case, the material properties undergo changes during the high temperature solar cell fabrication.

To clarify this point, experiments have been conducted to investigate the effect of high temperature treatment on the electronic properties of the ribbon. The bulk diffusion length of ribbons after high temperature (chosen near the junction diffusion temperature) annealing under neutral, oxidizing ambient, and phosphorous gettering conditions, was examined. The general conclusion is that the diffusion length of the bulk material degrades during high temperature treatment. In the case of phosphorous gettering, this degradation also depends on the gettering source and the gettering temperature. Thus, the eventual photovoltaic properties of EFG ribbon materials are not only dependent on the growth conditions, but also on the cell fabrication procedures. An optimum fabrication process should be considered as an integral part of the effort to maximize the quality of EFG ribbon as a photovoltaic material.

3. Cell Evaluation

Two series of growth experiments have been performed in furnace system No. 1: (a) variable purge rate growth, and (b) ambient gas mixture growth.

a. Solar Cell Results for Ribbons Grown in Variable Purge Rate Growth Experiments

Runs 18-153 to 18-159 were a series of growth runs to test the effect of reducing the main zone purge rate on the grown ribbon. Solar cell data are listed in Table III. Samples from runs 18-153 and

Table III. Summary of Solar Cell Data for Ribbons Grown from Various Reduced Ambient Conditions.

ELH Light, 100 mW/cm^2, 28°C, Cell Area = 55 cm^2

Run No.	J_{sc} (mA/cm^2)	V_{oc} (Volt)	FF	η (%)	Notes
153-1	16.42	.512	--	--	Contact
-2	17.60	.533	--	--	problem
154-1	17.82	.517	--	--	
155-1	18.10	.550	.696	6.92	
-2	17.28	.545	.711	6.70	
-3	25.40	.559	.690	9.77	} AR coated
-4	23.30	.552	.710	9.15	
156-1	17.72	.549	.717	6.98	
-2	16.70	.535	.701	6.27	
-3	24.00	.555	.700	9.27	} AR coated
-4	22.50	.541	.710	8.60	
159-1	17.47	.551	.735	7.08	
-2	23.80	.556	.720	9.57	AR coated

18-154 encountered some problems during the fabrication procedures, resulting in a poor fill factor. Otherwise, the cells all showed reasonable output and no significant differences between individual runs were seen. Judging from the short circuit density response, it is likely that the ribbon quality is still limited by the material bulk diffusion length. However, one distinct feature of this series of runs was that the cell samples frequently contained regions of large crystalline grains. In most cases, according to the IR scan measurement, the diffusion length of the large grain portions has approximately the same averaged bulk diffusion length of the whole cell. The only exception is run 18-150.[2] As shown in Fig. 7a, there are two large grain regions in cell 150-4. The diffusion lengths were determined to be 41 and 57 µm, while the whole cell average was 36 µm. In Fig. 7b, we also show a similar scan across a regular small grain portion of cell 150-5 for comparison.

b.   Ambient Gas Mixture Growth Experiment

In this series of experiments, various types of gases, such as CO_2, CO, and CH_4, have been introduced into the furnace by mixing with the argon carrier during the course of ribbon growth. Solar cell evaluation data for these experiments are summarized in Table IV. Judging from these results, the beneficial effects of the gas ambients, which are so apparent from the SPV diffusion length measurements, are not necessarily translated into equally improved solar cell performance.

The discrepancy between the high diffusion lengths found in these ribbons and the generally disappointing solar cell efficiencies had led to the speculative conclusions that the electronic properties of these ribbons change during the high temperature heat treatment of the solar cell fabrication. Experiments to test this hypothesis have therefore been initiated.

4.   Effect of High Temperature Treatments on Grown Ribbon

Several experimental investigations have been carried out to examine the effect of high temperature annealing on the electronic properties of the grown ribbon. The temperatures were chosen near the diffusion temperature for junction formation. The ambient gases were chosen with neutral, oxidizing, and getter conditions during the annealing. Experimental procedures were as follows:

(a) Cell 150-4

$L_n = 41\ \mu m$ $L_n = 57\ \mu m$

Large Grain   Large Grain

$L_n = 32\ \mu m$
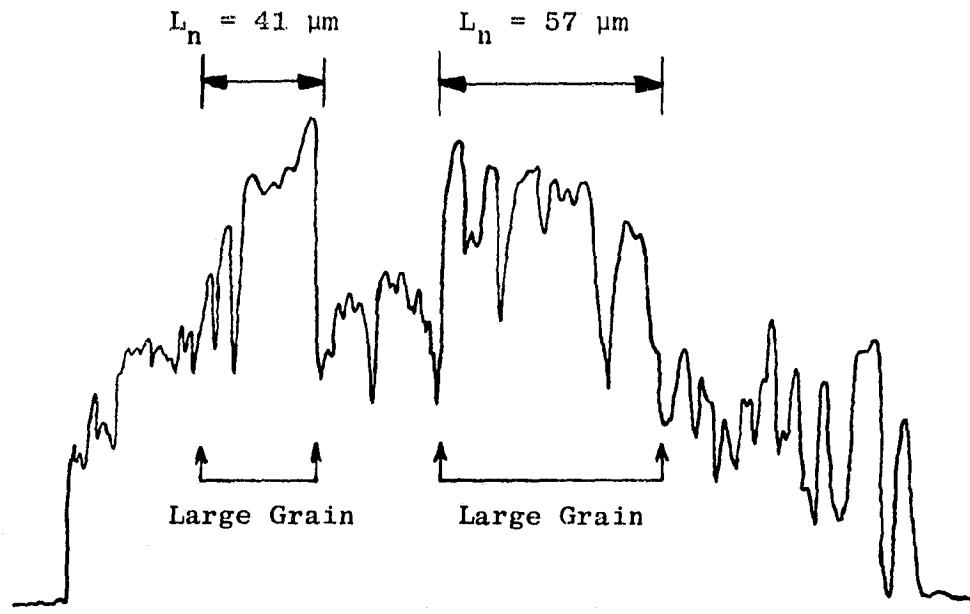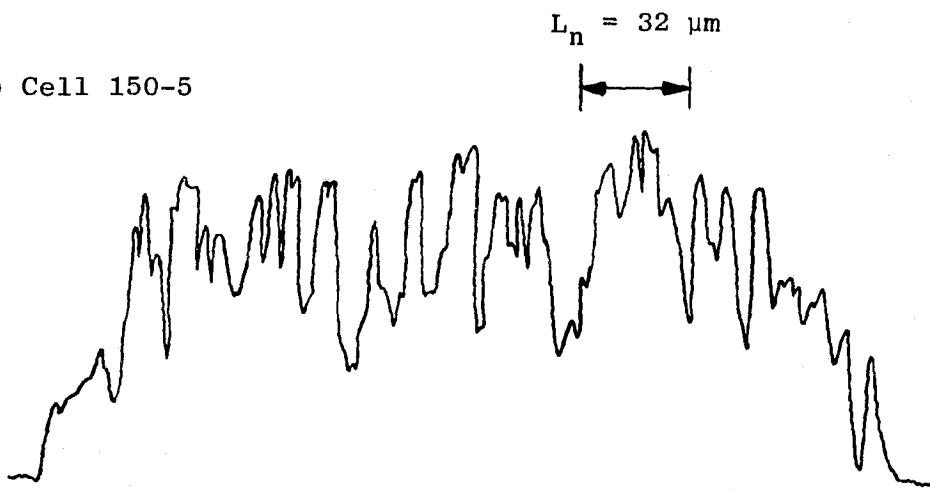
(b) Cell 150-5

Fig. 7. Comparison of IR scan spectra for (a) cell 150-4 which contains large crystalline grain regions, and (b) cell 150-5 which contains regular size of grain regions. The diffusion length in each grain region is also indicated.

Table IV. Summary of Solar Cell Output Data for Ribbons Grown Under Various Gas Ambients.

ELH Light, 100 mA/cm^2, 28°C, Cell Area = 55 cm^2, No AR*

Run No.	Growth Gas Ambient	J_{sc} (mA/cm^2)	V_{oc} (Volt)	FF	η (%)	Notes
18-170	CO_2 On	17.5 17.9	.543 .544	.698 .684	6.6 6.7	
18-171	CO_2 Off	16.4 17.3 17.6 17.6 17.4 17.5 17.8 17.5 17.3	.533 .542 .543 .544 .542 .538 .544 .540 .546	.738 .704 .718 .718 .702 .709 .747 .710 .679	6.4 6.6 6.9 6.9 6.6 6.7 7.2 6.7 6.4	
18-174	CO On	17.2 17.8 17.8 17.5 17.3	.531 .507 .538 .541 .539	.717 .466 .678 .713 .708	6.6 4.2 6.5 6.7 6.6	
	CO Off	16.8 16.8 17.1 17.7 16.6	.541 .531 .538 .539 .536	.693 .704 .742 .708 .661	6.3 6.3 6.8 6.5 5.9	
18-176	CH_4 On	18.3 18.0 17.2 17.4 17.6	.535 .541 .530 .544 .542	-- -- -- .729 .742	-- -- -- 6.9 7.1	} Contact problem

*Experience indicates that AR coating adds 42 to 45% to the efficiency figures.

To create a baseline, 5 x 10 cm samples were chosen from that portion of run 18-176 which had not been treated with any gas, i.e., was grown from a graphite crucible under "standard conditions." Each sample was halved: one-half was left untouched ("as-grown" sample), and the other half was subjected to high temperature annealing. Annealing conditions were 1000^OC for one hour under either H_2 (neutral) or O_2 (oxidizing) ambient gas. After the annealing, the N_2 treated samples, together with the "as-grown" samples, were etched in 401 solution, and the O_2 treated samples were etched in 1:1 ($HF:H_2O$) solution. Finally, all the samples were simultaneously processed into the standard Al Schottky diodes, using the "JPL pattern." The SPV diffusion lengths of the experimental samples are compared as shown in Tables V and VI. It appears that there is at least ~30% deterioration in the ribbon bulk diffusion length L_n after the high temperature treatment. Also, the particular ambient used in the anneal does not have a strong influence on the degradation mechanism.

a. Heat Treatment with Phosphorous Gettering Condition

The experimental samples were selected from a baseline run, 18-167. Two schemes of phosphorous gettering were adopted for this study. The first was to use PH_3 and O_2 gas mixtures forming a phosphorous glass layer, as normally used in a junction diffusion, and the annealing temperatures were ranging between 900^OC to 1000^OC. The other scheme was to use PH_3 and SiH_4 mixtures forming a doped oxide layer at 400^OC. Then the samples were annealed between 950^OC to 1050^OC, in N_2 ambient. The bulk diffusion lengths, as a function of annealing temperatures, were measured from the junction photocurrent response at long wavelength light, $\lambda = 1.0$ µm. As is shown in Fig. 8, the ribbon bulk diffusion lengths decrease as the annealing temperatures increase for both gettering schemes. But, in the second gettering scheme, L_n decreases at a slower rate than the first one. This series of experiments again demonstrated that there is a degradation of the ribbon bulk diffusion length after high temperature annealing.

B. Materials Characterization (J.F. Long)

1. Overview

At the beginning of this annual reporting period, a new routine characterization scheme was developed and implemented. The program in-

Table V. Summary of Annealing Experiment in N_2
Ambient. Furnace 18 Ribbons Grown
with Graphite Crucible.

Sample No.	Annealing Condition	Position	L_D (μ)	Deviation (μ)
18-176-1C	As-grown	A1	19.6	0.9
		A2	26.7	0.8
		A3	24.1	0.8
		A4	16.6	0.8
		A5	23.7	1.0
		Average:	22.1	
	1000^OC, 1 hr, N_2	B1	15.3	0.7
		B2	19.8	1.1
		B3	19.5	0.8
		B4	14.5	0.4
		B5	12.1	0.6
		Average:	16.0 (-28%)	
18-176-1J	As-grown	A1	25.3	1.8
		A2	28.9	1.2
		A3	23.7	0.7
		A4	24.3	0.7
		A5	24.9	0.9
		Average:	25.4	
	1000^OC, 1 hr, N_2	B1	14.6	1.2
		B2	7.7	0.8
		B3	21.5	1.2
		B4	20.9	0.7
		B5	6.6	0.8
		Average:	14.3 (-44%)	

Table VI. Summary of Annealing Experiment in O_2 Ambient. Furnace 18 Ribbons Grown with Graphite Crucible.

| Sample No.	Annealing Condition	Position	L_D (μ)	Deviation (μ)
18-176-2H	As-grown	A1	19.2	0.5
		A2	35.5	0.9
		A3	36.5	1.1
		A4	25.9	1.3
		A5	36.6	1.3
		Average:	30.7	
	$1000^{\circ}C$, 1 hr, O_2	B1	15.5	0.8
		B2	21.4	0.8
		B3	34.4	0.9
		B4	26.1	0.9
		B5	12.0	0.8
		Average:	21.9 (-29%)	
18-176-3H	As-grown	A1	14.5	0.5
		A2	28.1	1.2
		A3	40.8	1.0
		A4	32.4	0.9
		A5	12.4	0.4
		Average:	25.6	
		B1	4.4	0.5
		B2	31.4	1.4
		B3	25.2	0.7
		B4	18.8	0.6
		B5	9.2	0.5
		Average:	10.6 (-59%)	
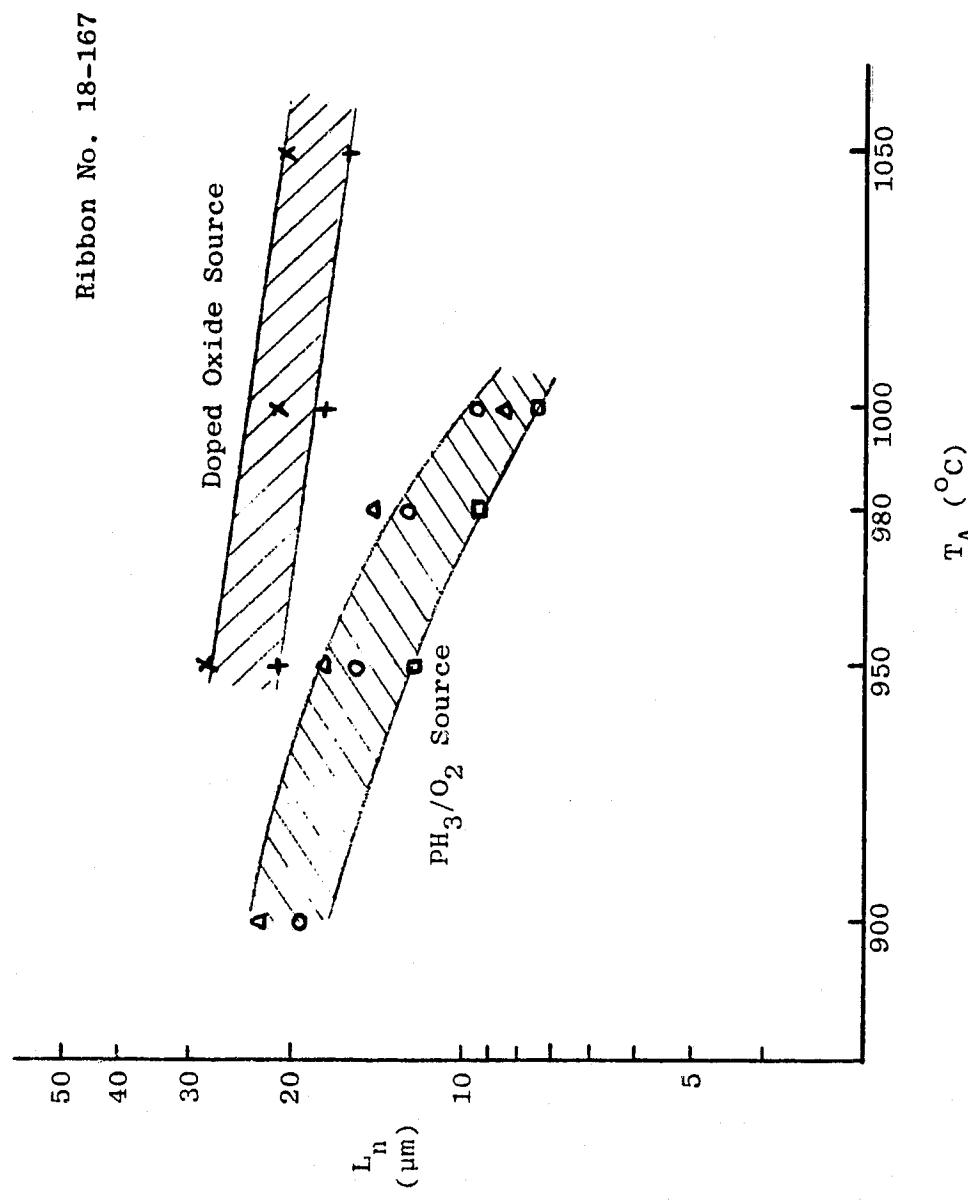
Fig. 8. Effects of phosphorous gettering source and temperature on the bulk diffusion length of graphite-grown RH-EFG ribbon.

volved the run-by-run monitoring of ribbon resistivity and type (via four-point probing), majority carrier mobility and concentration (via Hall/Van der Pauw), bulk minority carrier diffusion lengths and their spatial distribution (via the surface photovoltage or SPV technique), and continuous spatial current response induced by a 1 μm light source through which the samples were scanned. Evaporation masks for the fabrication of Schottky barriers were designed to accommodate both 5 cm wide and 10 cm wide ribbons (Fig. 9). Due to time and manpower constraints, aspects of this program were modified, such as the abandonment of the Hall/Van der Pauw measurement (good agreement had been found between Van der Pauw and four-point probe resistivities), and the reduction of emphasis on the infrared line scan measurement.

The SPV method, which became the primary characterization tool used, underwent modifications in the data reduction process which increased the accuracy of the method. These changes were based on (i) the recalibration of the apparatus' photodiode, (ii) more accurate correction for the spectral dependence of the optical transmission of the aluminum Schottky barrier, and (iii) the adoption of a non-linear curve fitting scheme for data analysis. These modifications eliminated the physically meaningless occurrence of negative values of diffusion length, and resulted in an average increase of approximately 8 μm over the values obtained via the old data reduction scheme.

Based largely on the SPV diffusion length results, it can be said that, for both Furnaces 1 and 3A, significant improvement was made in this annual period. In Furnace 1, average diffusion lengths reached a peak in the 40 to 60 μm range within a matrix of ambient and gas flow experiments. Furnace 3A achieved a peak average of approximately 25 μm in single cartridge, 5 cm growth, and closely approached that during a very successful five-cartridge run.

2. Furnace No. 1

Early in this annual period, a series of runs was undertaken utilizing a side channel die for the purpose of demonstrating fluid flow induced impurity redistribution. Undoped, boron doped, and aluminum doped material was grown. The results clearly demonstrated the redistribution phenomenon (see Figs. 6 and 7 of Ref. (3)).

Several runs were undertaken to determine the effects of various furnace components on material quality. This series of runs included the inclusion or omission of a cold shoe as well as the use of both gra-
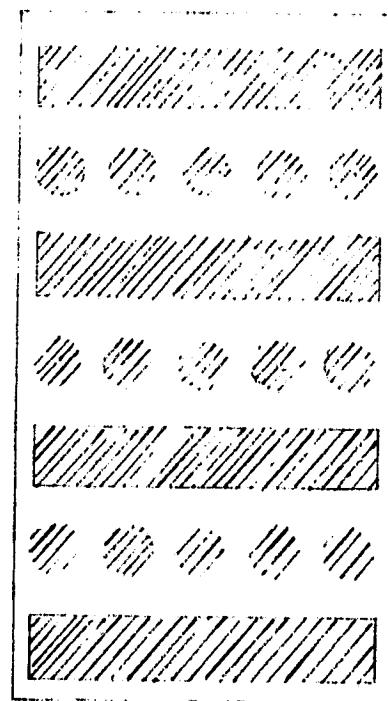
(a)
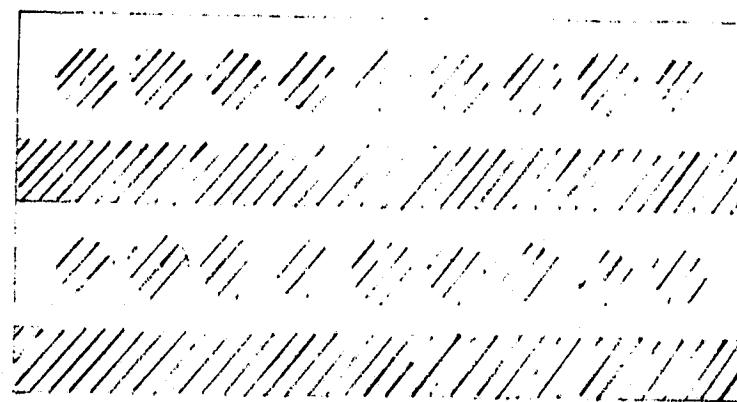
(b)

Fig. 9. Aluminum Schottky barrier deposition patterns for spatial characterization of (a) 5 cm, and (b) 10 cm wide ribbons.

46

phite and molybdenum insulation. Diffusion length averages for these
runs indicate that, at the level then achieved ($\bar{L}_D$ < 30 μm), the changes
had no first order effects.[3]

Another set of experiments dealt with modifications of the die top
geometry. A series of runs employed displaced dies for which the top
slot had been radiused, as well as opened up nonuniformly in the thick-
ness dimension. Again, no significant improvement (or degradation) in
material quality was observed as a function of any of these changes.[2]

Experiments in which the main zone ambient was altered led to the
most significant improvement in minority carrier diffusion length aver-
ages. The reduction of the main zone argon purge rate, which was accom-
panied by a build-up of surface film on the ribbon, resulted in average
diffusion lengths in the 30 μm range at first. Ultimately, as the con-
trol of the experimental conditions was refined, diffusion length aver-
ages were routinely in the 40 μm range (Table VII). Characterization of
the film indicated that it is composed of SiC and SiO or SiO_2.[2] It
was also noted that, in the presence of the film, the incidence of SiC
particle inclusions is greatly reduced. The effect of operation with
and without a cold shoe was again examined within the matrix of purge
rate reduction experiments. Growth speed was also considered as a
parameter. There appears to be the suggestion that the presence of the
cold shoe may be slightly detrimental to material quality (Table VII).

The most recent set of experiments involved the introduction of
various gaseous species onto the growth interface via the use of gas
jets. These experiments comprised an attempt to better understand the
mechanism of film formation. The three gases involved were CO_2, CO, and
CH_4 (see Section II for a more detailed discussion of the rationale).
Table VIII is a summary of the diffusion length averages for each sample
under varying flow rates of the particular jet gas. It appears from
these results that, at least in the cases of CO_2 and CO, significant im-
provement in diffusion length results from the introduction of these
gases onto the interface. The case for methane is less clear. It has
been noted that a film build-up accompanies the introduction of these
gases. In the CO_2 and CO cases, the film appears to be similar to that
obtained in the ambient flow reduction experiments. In the instance of
methane, however, the film has been identified as entirely SiC. In all
of these cases, the incidence of SiC particle inclusions again is greatly
reduced.

47

Table VII. Diffusion Length Averages for Series of Runs Involving Variable Main Zone Purge Rates.

Run No.	$\overline{L}_D$ (µm)
18-153[†]	31.7
-154	49.3
-155	44.7
-156	39.7
-157*	42.5
-158	47.6
-159	31.7
-160[††]	48.6
-161**	26.5
-162**	35.1
-164**	26.0
-165	20.9
-166	29.6
-167	23.2
-168	41.9
-169	32.2

[†]Non-displaced die.
*Only one sample examined.
[††]Float-zoned silicon as charges; undoped.
**Cold shoe run.

Table VIII. Summary of Series of Runs Involving Introduction of Various Gaseous Species via Gas Jets.

Sample No.	Main Zone Purge Rate (ℓ/min)	Jet Gas	Jet Gas Flow Rate (cc/min)	$\overline{L}_D$ (μm)
18-170-1F	10	1% CO_2 in Ar	0	33.9
-1H	10	"	400	48.7
-3F	10	"	200	48.2
-4A	10	"	200	48.8
-4G	10	"	500	48.9
-5B	10	"	0	42.3
-5E	10	"	0	34.9
18-171-1B	10	"	0	36.5
-3E	10	"	0	35.5
-4D	10	"	400	37.5
-5D	5	"	400	49.0
-5I	5	"	400	45.0
-7I	5	"	0	35.3
-8D	2	"	0	34.8
-8H	2	"	3000	48.3
18-172-1G	3	"	200	39.5
-1H	3	"	200	35.1
-1M	3	"	200	46.0
-2D	4	"	150	46.7
-4D	4	"	150	30.2
-4G	4	"	150	41.7
-4L	4	"	150	46.3
18-173-1E	10	Ar	4000	20.1
-1I	10	5% CO in Ar	4400	30.6
-1L	10	2% CO in Ar	4200	33.5
-2H	10	1% CO in Ar	4100	40.1
-2L	10	"	4100	39.8
-3G	10	"	4100	36.8

Table VIII Continued.

Sample No.	Main Zone Purge Rate (ℓ/min)	Jet Gas	Jet Gas Flow Rate (cc/min)	$\overline{L}_D$ (μm)
18-174-1G	10	.6% CO in Ar	2000	34.3
-2B	10	.2% CO in Ar	2000	46.4
-2D	10	.2% CO in Ar	2000	48.7
-2I	10	<.1% CO in Ar	6000	40.2
-2L	10	<.1% CO in Ar	6000	35.8
-3L	10	Ar	1000	22.1
-4I	10	1% CO in Ar	2100	49.0
18-175-1B	10	Ar	4000	26.9
-2B	10	Ar	4000	37.9
-2D	10	<.1% CH_4 in Ar	6000	47.3
18-176-1B	3	.2% CH_4 in Ar	0	25.5
-1J	3	"	0	27.9
-3G	10	"	0	29.9
-5E	10	"	4000	28.9
-5H	10	"	4000	31.4
-5J	10	"	4000	31.4
-5L	10	"	4000	35.0

50

In any case, the reduction of main zone purge as well as the introduction of these gases have resulted in the highest diffusion length averages obtained to date on material from JPL Furnace No. 1.

3. Furnace No. 3A

The series of runs undertaken early in this annual reporting period (16-155 to 16-171) involved modifications to die geometry in an attempt to achieve good growth stability and electronic quality. It was during this testing that displaced dies were found to result in higher diffusion length averages, as well as reduced SiC particle densities.[6]

Runs 16-172 to -177 were developmental in nature, designed to test the melt replenishment scheme, and leading to multiple cartridge operation. With run 16-172, the long hot zone was installed. Runs 16-172, -173, and -174 were undoped, yet the low resistivity values (5.3, 0.5, and 13.5 Ω-cm, respectively) reflect the overall level of contamination in the system. None of these runs produced any material of reasonable electronic quality.[3]

Run 178, immediately following the first multiple run, was single cartridge without melt replenishment. Minority carrier diffusion lengths were high again; in fact, the best achieved to this point in Furnace 3A. Run 179, in which the replenisher was reinstalled, recreated these conditions.[3] Run 180, the second multiple run attempt, was plagued with high SiC particle densities and the diffusion length averages were correspondingly depressed.

The next series of runs (181-187), which led up to the successful multiple ribbon demonstration, contained several experiments of a developmental nature. Run 184 successfully demonstrated cycled melt replenishment and intermittent doping over an 18 hour period (Fig. 10). Run 185 employed silicon chips of questionable purity to augment the solid charge, and observations indicated low resistivity and diffusion length which rose with time.[2] Run 186 employed a used crucible in a successful attempt to reduce SiC particle densities. Run 187 demonstrated the successful culmination of this series of runs with multiple ribbon growth of material of electronic quality comparable to any material produced in Furnace 3A to date (Fig. 11). Table IX summarizes the conditions and diffusion length averages for this series of runs.

The latest series of runs examined (197 to 200, 205 to 206) followed a long series of developmental runs for 10 cm wide growth (for which no material was examined). Each of these runs was single cartridge; all em-
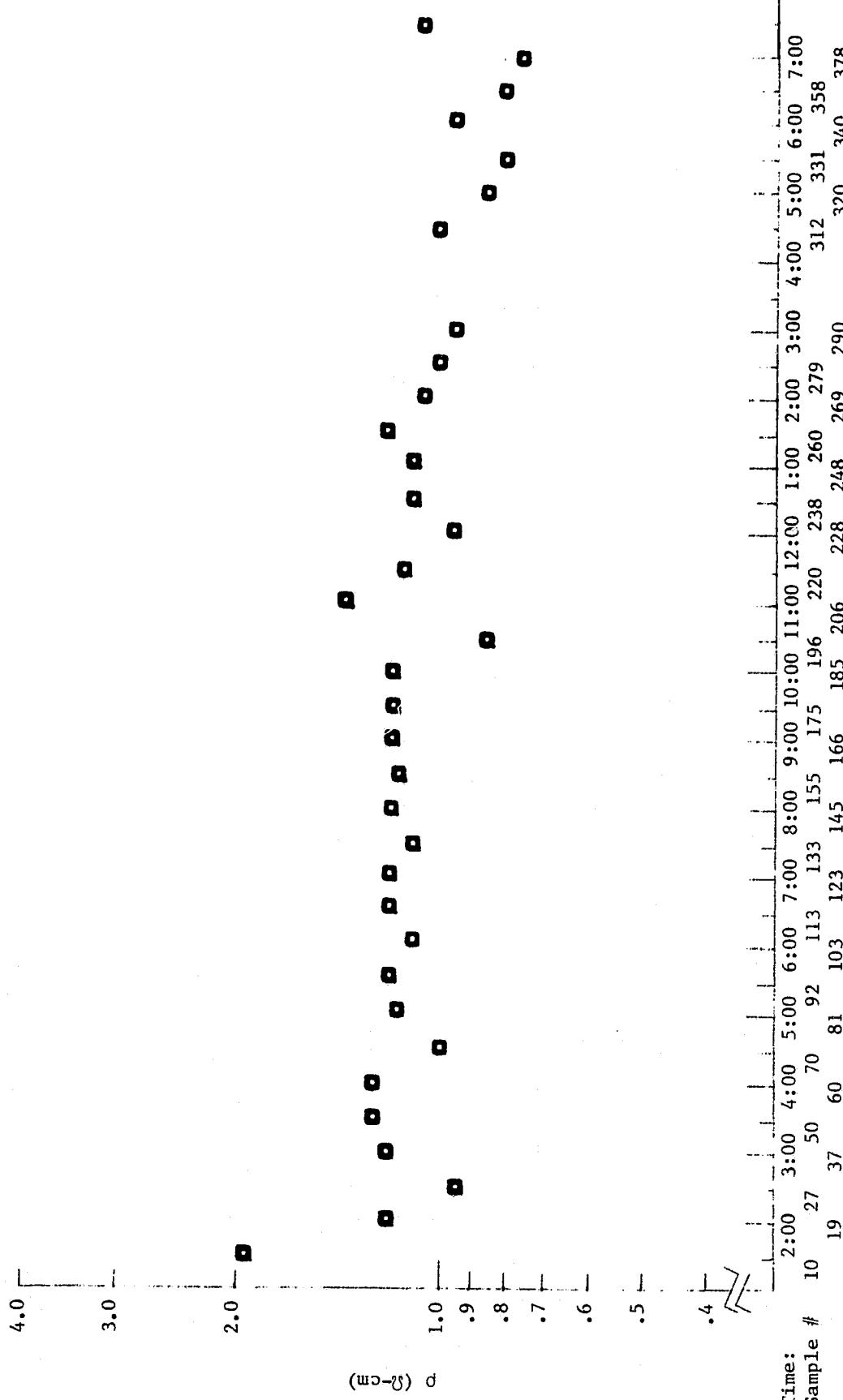
Fig. 10. Four-point probe resistivity vs. run time for intermittent doping replenishment demonstration run No. 16-184.

52

Cartridge #	L_D (µm)
● 1	24.4
○ 2	19.7
▲ 3	20.4
△ 4	20.1
+ 5	22.2
Overall	21.3

Run Time: 10:00 12:00 2:00 4:00 6:00 8:00 10:00 12:00 2:00
a.m. p.m.
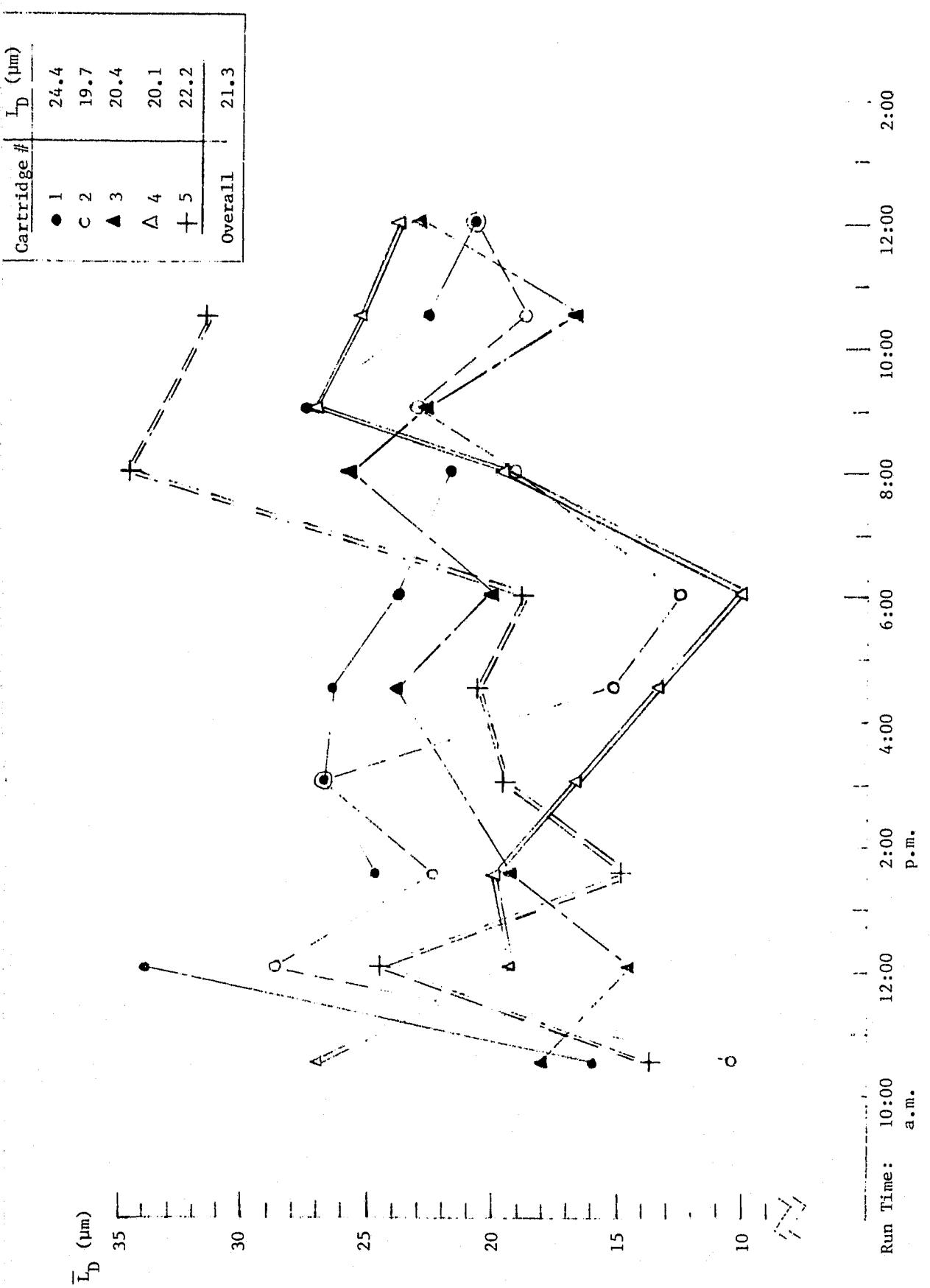
Fig. 11. Minority carrier diffusion length (sample averages) vs. run time
for multiple growth run No. 16-187.

53

Table IX. Summary of Series of Runs Leading to
Successful Multiple Ribbon Growth
Run No. 16-187.

Run No.	Experimental Conditions	$\overline{L}_D$ (μm)
16-181	Single Cartridge; developmental; not strictly clean; high SiC particle densities.	7.1
16-184	Single cartridge; 18-hour cycled melt replenishment.	19.2
16-185	Multiple cartridge; silicon chips in charge; L_D rises with time.	15.4
16-186	Single cartridge; used crucible; very low SiC particle densities.	
16-187	Multiple cartridge (see Fig. 11).	21.3

ployed melt replenishment. Table X is a summary of minority carrier diffusion length averages for this series. With the exception of run 200, each of these runs displayed a "frowning" spatial diffusion length distribution (e.g., 197, Fig. 12). Run 16-200 displayed a distinct diffusion length "hole" centered on every sample examined (Fig. 13). Examination of the die after the run revealed evidence of a large void occupying most of the saw cut. This void undoubtedly produced atypical fluid flow conditions and a resultant impurity distribution reflected in the observed spatial diffusion length distribution. Run 205 was aluminum doped, with a measured average resistivity of 4.8 Ω-cm. The aluminum was introduced late in the run, which had been boron doped (the initial boron concentration was allowed to deplete via undoped replenishment). The sample average resistivity is shown to decline slightly with time, as the aluminum is added:

Sample No. (Shown Chronologically)	ρ (Ω-cm)
8	5.6
7	5.1
6	5.0
5	4.7
3	4.2
1	4.4

The spatial distribution of resistivity was found to have an overall "frowning" shape as well. Run 206, which was boron doped, again displayed the "frowning" diffusion length distribution typical of 10 cm ribbon to date.

Table X. Summary of Minority Carrier Diffusion Lengths
for 10 cm Ribbon Series of Runs.

| Run No.	Experimental Conditions	$\overline{L}_D$ (µm)
16-197	Single cartridge; melt replenished; not strictly clean.	14.4
16-198	Single cartridge; melt replenished; not strictly clean.	18.4
16-199	Single cartridge; melt replenished; not strictly clean.	13.7
16-200	Single cartridge; melt replenished; void noted in saw cut die (see text).	11.7
16-206	Single cartridge; melt replenished; not strictly clean.	11.7
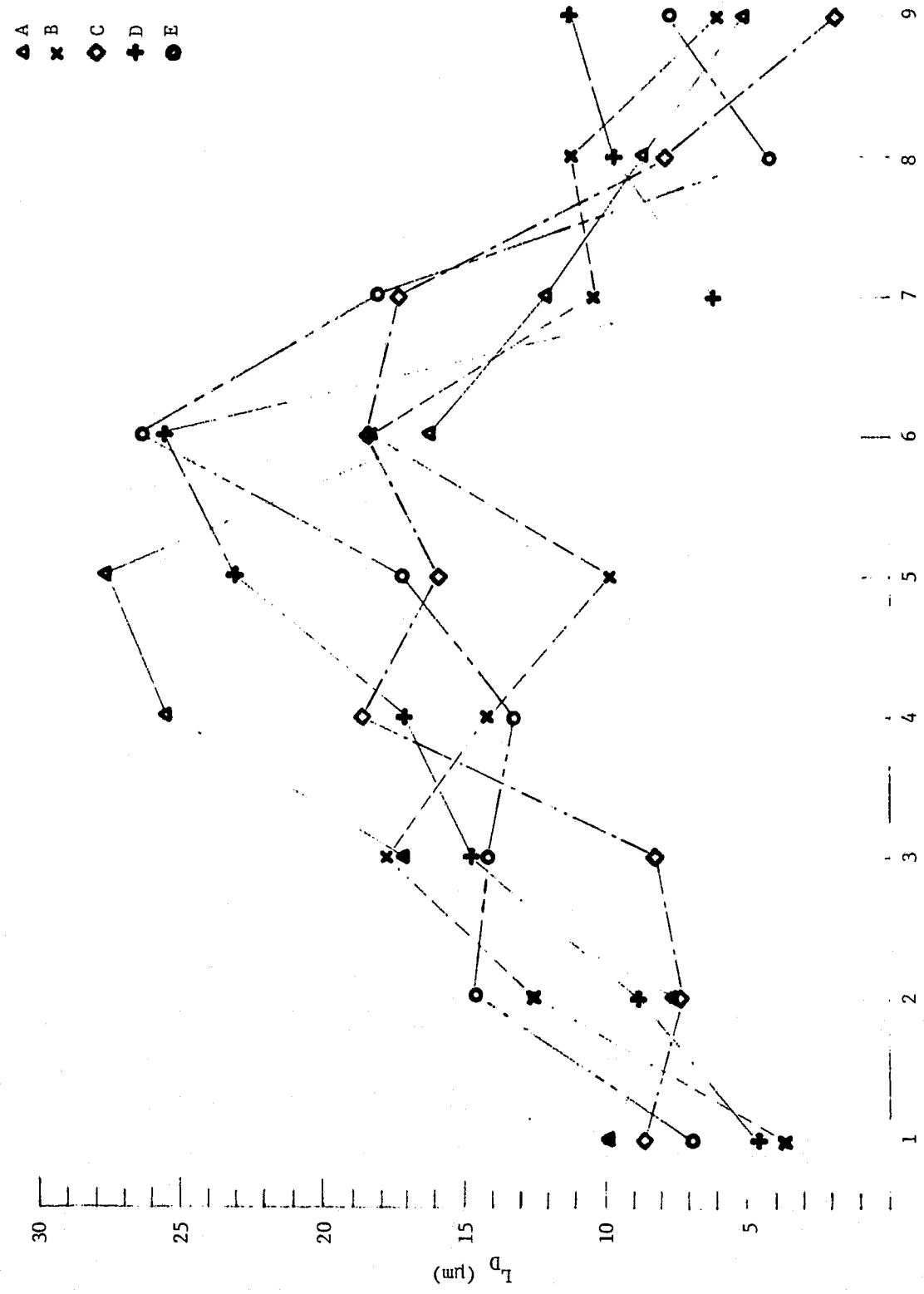
Fig. 12. Spatial distribution of minority carrier diffusion length, run No. 16-197.

57
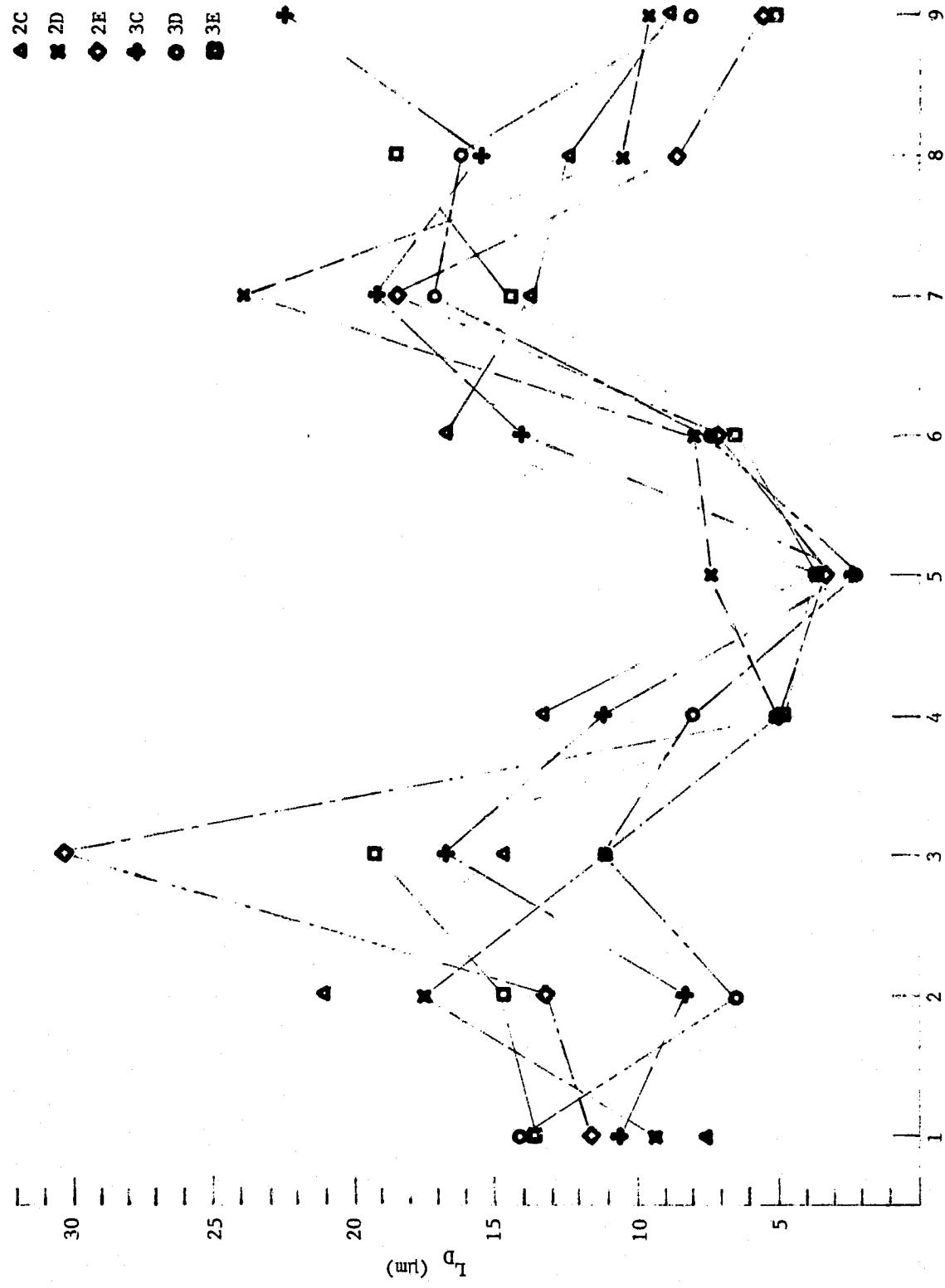
Fig. 13. Spatial distribution of minority carrier diffusion length, run No. 16-200.

V. FURNACE 17

A. High Speed Growth of Ribbon (J.P. Kalejs)

1. Overview

The problems of stress and deviations from ribbon flatness of 7.5 cm wide ribbon grown in high speed systems (3 to 5 cm/min) have been investigated in a series of experiments carried out in Furnace 17 in the past year. Considerable effort was spent initially in improving ribbon guidance. This helped to minimize perturbations due to interference between the ribbon and the growth slot walls and allowed more meaningful experiments to be planned to study the effects of changes in the cooling profile on ribbon stress levels. Baseline stress distributions for ribbon grown at reduced speeds (~2 cm/min) in a 7.5 cm cartridge without a cold shoe were first examined for a number of different cooling profiles. The latter was altered by changing both the afterheater geometry and its operating temperature. Additional experiments with a higher speed growth system which contained cold shoes added to the range of cooling profiles studied. In this second phase of the work, the ambient was utilized to influence the ribbon thermal environment in the use of nonuniform gas flow distribution while at the same time varying the ambient composition (argon vs. helium) to change its thermal conductivity.

Measured stress levels were observed to respond to changes in the ribbon cooling profiles in a number of the situations examined. However, a consistent picture of differences in ribbon stress between the low and high speed growth systems has not emerged from these studies. Ribbon grown at speeds of 5 cm/min remained reasonably flat, while measured stress levels at the highest speeds did not increase significantly over those typical at about 2 cm/min in the low speed growth system. In general, the deviations of the ribbon from flatness did not noticeably per-

turb steady-state growth even in the most extreme case of the ribbon grown at 5 cm/min.

2. Experimental Work

Experiments with the 7.5 cm growth system were concluded during the first part of this quarter. The main purpose of this work was to evaluate high speed (up to 5 cm/min) growth conditions without cold shoe gas flow and for several cold shoe openings. Most of the quarter was spent in conversion of Furnace 17 to accommodate the 10 cm cartridge. This included modifications to system power supplies and control elements. After several preliminary growth attempts to evaluate system component performance were made, growth of full width (10 to 11 cm wide) ribbon at speeds up to 4 cm/min has been demonstrated. The experimental work is discussed in more detail below.

a. 7.5 cm Cartridge

The evaluation of high speed growth conditions without the aid of cooling gas to the cold shoes was carried out in conjunction with cold shoe modifications designed to increase the temperature gradient at the growth interface. The latter was accomplished by decreasing the extent of the separation of the cold shoes and the die top, and by reducing the gap between the cold shoes.

At the smallest cold shoe-die top separation of 0.08 cm and narrowest cold shoe gap of 0.09 cm, growth was not possible because available face heater power was not sufficient to overcome the heat losses due to increased cooling of the die top by the cold shoes. Maximum growth speeds of 4.8 cm/min were demonstrated without gas cooling at a greater gap spacing of 0.125 cm. However, growth conditions were generally poor. Precise centering of the cold shoes, as well as tolerances on their dimensions, were felt to be factors in the ability to reproduce growth conditions in these extreme configurations. Reasonable full width growth conditions were achieved at a gap spacing of 0.15 cm. Steady-state growth of reasonably flat ribbon, with thicknesses in the range from 0.02 to 0.03 cm, and at speeds of 4.0 to 4.2 cm/min was demonstrated to be feasible without gas flow to the cold shoes. Stress levels in the ribbon and flatness were found to be comparable to those reported for this cartridge system in a previous quarterly.[3]

b. 10 cm Cartridge

Growth with the 10 cm cartridge was carried out in Furnace 17 with essentially the same system used in the development work in Furnace 3A reported in Section III. Initial runs revealed deficiencies in Furnace 17 power supplies and the video system which required correction. Several combinations of different length end heaters and nonuniform cross-section face heaters were evaluated in conjunction with a graphite die-top shield. The ease of spreading and full-width growth were found to respond to changes in the die-top thermal profile effected by changes in the heater design. Optimization of growth conditions was not sought in these preliminary runs because the design of other system components, particularly the shield and die, also is a consideration in such work. This effort will be continued after Furnace 17 is cleaned up for quality work.

All the growth done to date with the 10 cm cartridge in Furnace 17 has been without gas flow to the cold shoes. Maximum growth speeds for which full-width steady-state growth could be maintained under these conditions were in the range from 3.8 to 4.2 cm/min. Ribbon thickness at the higher speeds was in the range from 0.02 to 0.03 cm. These values are in the same ranges obtained, also without gas flow to the cold shoes, in the 7.5 cm cartridge system. Stress levels and ribbon flatness were also observed to be comparable.

B. Automatic Controls (B. Mackintosh

1. Overview

Work done in the past year in the area of automatic control of ribbon growth falls primarily under two headings, namely a study of meniscus dynamics, and development of video analysis hardware. The study of the dynamics of EFG and means of effecting closed-loop control over the process, were subjects for which Furnace 17 was specifically designed. The key elements of the special equipment on this station, i.e., the anamorphic optical system, TV camera, and instrumentation systems, have been adequately described in previous reports. A 7.5 cm cartridge was operated in this furnace during the time this work was in progress.

2. EFG Dynamics Study

This work is reported in detail in the Second Quarterly Report.[2] A brief review is as follows. The equations describing the

meniscus geometry and heat balance of the EFG process were linearized
about an operating point to yield second-order differential equations.
From these equations were derived the natural frequency and damping ratio
of response of the meniscus height and ribbon thickness to changes in die
temperature and pulling speed, for given initial or steady-state values
of these parameters. The dynamic relationship between power input to the
die heater and the temperature of the die top was then derived from a
lumped-parameter model of these system elements. These two models were
then verified experimentally, using the various instrumentation features
of Furnace 17, by the method of frequency response. Both the linearized
meniscus dynamics and the heater power-die temperature models were proven
by these frequency-response measurements to be accurate. A final set of
measurements was made to verify the dynamic relationship between varia-
tions about an operating point of the die heater power and the meniscus
height, a relationship which combines the dynamics of the two models de-
scribed above.

This study yielded information upon which an optimum control system
could be designed to control ribbon thickness or meniscus height by act-
ing upon either pulling speed or heater power. It did not, however,
treat the question of response of ribbon edge position to these inputs.
Control of edge position is a problem of equal importance in EFG ribbon
growth. It is therefore our plan to perform a similar study of the dy-
namics of edge-position response. Following this study, a complete con-
trol system can be designed to maintain ribbon width, and height of the
central-region meniscus within precise limits by controlling the three
die-region heaters and pulling speed. Carrying out this ribbon edge-
position response study was postponed until Furnace 17 was converted to
accept the 10 cm cartridge and until reliable and reasonably stable
growth of 10 cm ribbon was established. During this conversion period,
work in the area of automatic controls was concentrated upon developing
video signal processing circuitry.

The operation of Furnace 17 for more than a year has confirmed that
the system consisting of anamorphic optics, a TV camera, and appropriate
processing circuitry provides reliable, high-resolution information about
the positions of ribbon features. There is every indication that the
automatic growth control systems based on this combination of elements
will also be easy for production personnel to set up and operate. This
is true because all information necessary to properly adjust the sensing
system is presented on the television monitor, simultaneously with the

image of the growing ribbon. For these reasons, this TV camera-based sensor appears to be a good basis for automatic control of the process.

The work done to date with TV camera sensing of ribbon growth has entailed the use of purchased video-analysis equipment. We have begun developing our own circuitry for video-processing building blocks which can, as the requirements for ribbon growth control become better defined, be assembled into complete systems for multi-ribbon production units. The video processing circuitry now being designed, and an example of its use to derive three control signals from the image of a ribbon, are shown in Fig. 14.

Separate video and sync signals from the TV camera are applied to the processor. The video signal is passed through two comparators or quantizers so that the image of the ribbon edge-to-background transition, and that of the ribbon-to-meniscus transition in the center, can independently be adjusted for maximum contrast. The sync signals are furnished to three window generators, one for each ribbon feature. The "rectangular" windows generated by these timing circuits gate integrators which accumulate the total amount of white area in the scan line segments contained within the windows. A horizontal position adjustment for each edge window, and a vertical position adjustment for the center window, are provided for setup purposes. Finally, the video output to a monitor contains the sum of signals from the three window generators, plus the video signal from either of the two quantizers or the non-quantized video. In the form in which the circuitry is now being developed, the contents of each box represented in Fig. 14 are built on a plug-in circuit card.

A complete ribbon-growth control system will consist, additionally, of controller circuitry for each of the three channels illustrated, plus operator-interface circuitry. The nature of the controllers will be decided after the edge-position response study described above has been completed. The complete control system will then be developed to include optimum packaging, layout, and operator interface. The question of expandability for operation of multiple growth stations from a central point will also be considered.
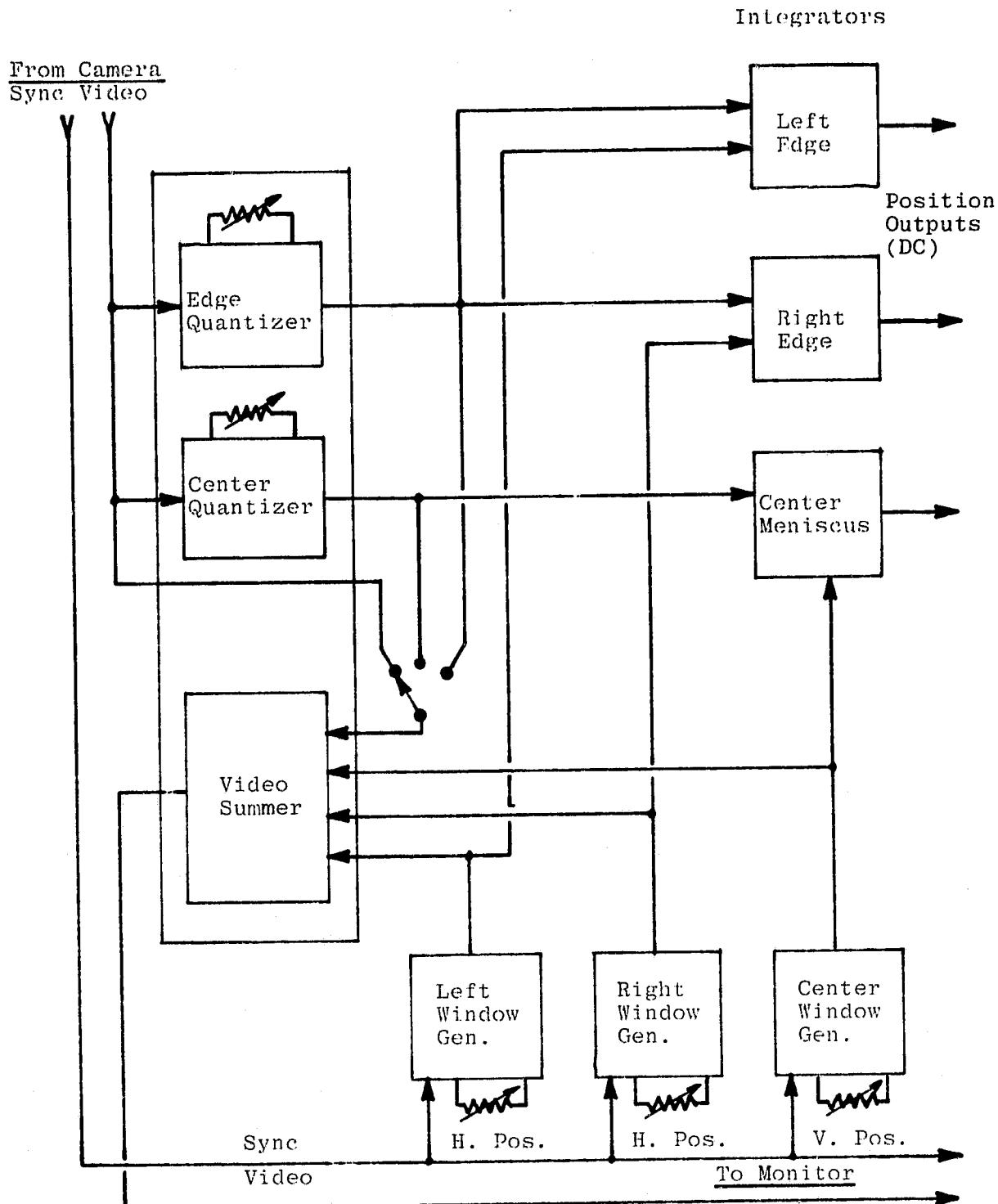
Fig. 14. Video analysis system for control of EFG ribbon process.

64

VI. REFERENCES

1. F.V. Wald et al., "Large Area Silicon Sheet by EFG," Annual Progress Report, DOE/JPL 954355/78-3 (September 1978).

2. F.V. Wald et al., "Large Area Silicon Sheet by EFG," Second Quarterly Progress Report, DOE/JPL 954355/79-2 (July 1979).

3. F.V. Wald et al., "Large Area Silicon Sheet by EFG," First Quarterly Progress Report, DOE/JPL 954355/79-1 (April 1979).

4. K.H. Yang and G.H. Schwuttke, Phys. Stat. Sol.(a) <u>48</u> (1978) 335.

5. F.V. Wald et al., "Large Area Silicon Sheet by EFG," Monthly Progress Report (February 1979), Subcontract No. 954355.

6. F.V. Wald et al., "Large Area Silicon Sheet by EFG," Fourth Quarterly Progress Report, DOE/JPL 954355/79-4 (January 1979).

APPENDICES

1. **Updated Program Plan**

   The original program plan, as amended, is still in effect.

2. **Man Hours and Costs**

   Previous cumulative man hours were 56,851 and cost plus fixed fee was $2,011,299. Man hours for fiscal year October 1, 1978 to September 30, 1979 are 21,458 and cost plus fixed fee is $749,115. Therefore, total cumulative man hours and cost plus fixed fee are 78,309 and $2,760,414, respectively.

3. **Engineering Drawings and Sketches Generated During the Reporting Period**

   Figs. 2 and 14.

4. **Summary of Characterization Data Generated During the Reporting Period**

   Tables A1 and A2, which present data on the 5 cm multiple demonstration run. See also Section IV.

5. **Action Items Required by JPL**

   None.

6. **New Technology**

   Several of the efforts here have generated items of potentially "new" technology. Some have been separately reported pending possible patent action, and all are being scrutinized for the same purpose.

Table A1. Multiple Growth Demonstration Run No. 187
Solar Cell Performance Data.

Cell No.	J_{sc} (mA/cm^2)	V_{oc} (Volt)	FF	η (%)	Notes
187-1-1	23.30	0.527	0.699	8.63	
-2	23.20	0.531	0.695	8.56	
-3	22.79	0.531	0.673	8.15	
-4	23.26	0.536	0.687	8.56	
-5	24.43	0.545	0.713	9.49	Cartridge No. 1
-6	22.97	0.534	0.730	8.96	
-7	23.00	0.538	0.718	8.89	
-8	23.75	0.533	0.651	8.24	
-9	<u>23.18</u>	<u>0.532</u>	<u>0.700</u>	<u>8.63</u>	
Average	23.32	0.534	0.696	8.68	
187-3-1	23.37	0.531	0.731	9.06	
-2	23.89	0.536	0.705	9.03	
-3	23.67	0.541	0.711	9.12	Cartridge No. 3
-4	23.90	0.535	0.694	8.86	
-5	<u>23.14</u>	<u>0.542</u>	<u>0.729</u>	<u>9.54</u>	
Average	23.79	0.537	0.714	9.12	
187-4-1	22.64	0.523	0.689	8.15	
-2	23.14	0.528	0.684	8.37	
-3	23.54	0.530	0.701	8.74	
-4	22.77	0.534	0.736	8.96	Cartridge No. 4
-5	23.39	0.526	0.665	8.19	
-6	22.74	0.529	0.716	8.62	
-7	23.41	0.536	0.706	8.86	
-8	<u>22.56</u>	<u>0.536</u>	<u>0.706</u>	<u>8.53</u>	
Average	23.02	0.530	0.70	8.55	
187-5-1	23.74	0.534	0.672	8.52	Cartridge No. 5

Table A2.   Multiple Growth Demonstration Run No. 187
            Productivity Data.

Station No.	1	2	3	4	5
Total Quantity (meters)	30.4	29.6	29.9	31.1	27.7
Total Duration of Growth (minutes)	910	890	825	919	829
Percentage of 15.5-Hour Run Period* Actually Growing	97.8	95.7	88.7	98.8	89.1
Number of Freezes	3	5	6	3	4
Longest Duration of Continuous Growth (minutes)	692	331	505	490	508
Average Growth Rate (cm/minute)	3.34	3.33	3.62	3.38	3.34
Overall Duty Rate	.940				