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LARGE AREA SILICON SHEET BY EFG

Annual Progress Report, October 1, 1979—September 30, 1980

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Mobil Tyco Solar Energy Corporation
Waltham, Massachusetts

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Solar Energy

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Mobil Tyco Solar Energy Corporation
16 Hickory Drive
Waltham, Massachusetts 02254

LARGE AREA SILICON SHEET BY EFG

Program Manager: F.V. Wald

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ABSTRACT

This review of the past year's work concentrates on progress in the development of a cartridge system for growth of 10 cm wide ribbon. Growth speed capability, automated growth, ribbon quality and solar cell performance are areas in which significant progress is reported.

Routine growth of 10 cm wide ribbon at speeds in the range from 3.5 to 4.0 cm/minute has been demonstrated both in single cartridge and multiple ribbon furnaces. Simultaneous growth of three 10 cm wide ribbons over a period of several hours has also been accomplished. A system for automated control of ribbon width has been developed and successfully implemented in the multiple ribbon growth system.

As-grown ribbon quality and solar cell performance has continued to improve for the 10 cm wide ribbon grown in high-speed systems. Cell efficiencies of greater than 10% have been demonstrated on large areas ($\sim 50 \text{ cm}^2$) of this ribbon. Better optimized growth conditions and cell processing have now been combined to produce greater than 13% (AM1) small area ($\sim 6 \text{ cm}^2$) cells on ribbon grown at 2 cm/minute. Optimization work for 10 cm wide ribbon is continuing aimed at understanding the factors which affect quality in these systems. Utilization of computer modeling to study interface shapes and mass transport phenomena in the meniscus are part of this work.

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I. INTRODUCTION

In the past year, all essential elements have been demonstrated in accordance with the 1986 LSA project goals to qualify EFG multiple ribbon technology as a candidate for production of low-cost substrates for terrestrial solar cell fabrication. Solar cells of efficiencies over 13% have been prepared from resistance furnace-grown ribbon, 10 cm wide ribbon has been grown at speeds of 4 cm/minute, and automatic controls have been developed and successfully used during growth of 10 cm wide ribbon in a multiple ribbon furnace. It remains to integrate all these demonstrated elements into a single multiple-ribbon furnace for 10 cm wide ribbon that is the prototype unit of a large-scale facility for production of EFG silicon ribbon at the low costs necessary to achieve the LSA project goals. The milestone toward completion of the integration task scheduled for 1980, referred to as the "technical features demonstration," has not yet been achieved, however, and so the program is behind schedule. Nevertheless, the necessary information to accomplish this milestone has been gathered, and suggests that it can be achieved by design iterations on the equipment presently in use; that is, there is no technical basis for believing that the obstacles are of a fundamental nature. This view is better expressed by considering in more detail the progress that has been made in the various areas of development of the EFG prototype multiple growth units and related work.

By the end of 1979, the program had made significant progress toward a technology for production of silicon ribbon by the EFG technique that is capable of being scaled to levels required for low-cost substrates for solar cells. Growth of five ribbons, each 5 cm wide, with continuous melt replenishment for 15 hours was demonstrated, with a total output of 150 m of rib-

bon at speeds of 3.5 cm/minute and a machine duty cycle of over 90%. Growth of 10 cm wide ribbon in an upscaled version of the basic system had been shown to be viable, and the fundamentals of an automatic control system evolved to a point of understanding sufficient to permit construction of prototype units. Cell efficiencies up to 11.5% (AM1) had been demonstrated for large areas ($\sim 50 \text{ cm}^2$) for ribbon grown in single-ribbon (cartridge) furnaces at speeds of the order of 2 cm/minute, and cell efficiencies for ribbon grown in the more complex multiple-ribbon furnace at speeds of up to 4 cm/minute averaged 9%.

The work in the past year accordingly focused on development of a multiple ribbon system for 10 cm wide ribbon capable of growing three ribbons with continuous melt replenishment and automatic control capabilities, and on gaining further understanding of factors that influence material quality in high-speed growth. The technical features demonstration requirement for the multiple ribbon furnace for 1980 was for a run length of eight hours, a growth rate of 4.5 cm/minute, a machine duty rate of 85% or better, operational automatic controls on one ribbon, and a ribbon quality sufficient for a 10.2% cell efficiency. In addition, an efficiency-related goal of the demonstration of a 13+% cell was required. Significant developments related to the work toward these goals which occurred in this past year have been:

(i) Characterization and development of the 10 cm cartridge to gain a better understanding of the parameters that control the die top isotherms, hence growth stability and the maximum speed capability. Reproducible growth conditions and greatly increased stability and control over ribbon width have resulted, and growth at speeds of 3.5 to 4.0 cm/minute is routinely possible with a control level sufficient to make multiple ribbon growth feasible.

(ii) A complete automatic control system for ribbon width control has been demonstrated. It has been proven highly successful in routinely allowing growth of 10 cm wide ribbon over time spans of the order of hours with minimal operator intervention. This system has been now installed for use with all three 10 cm cartridges of the multiple-ribbon furnace.

(iii) Improvements of cell efficiencies to the range of 10 to 11% have been demonstrated for 10 cm wide ribbon grown at speeds of up to 4 cm/minute. Although all factors relevant to quality improvement at higher speeds are not yet understood, the ambient composition influence demonstrated in a lower speed growth system, and which has now been used to achieve cell efficiencies over 13% there, has also been shown to be operative in the case of higher speed growth. Optimization of these effects and study of additional factors which may have an important influence has proceeded through the utilization of computer modeling to study interface shape effects and mass transport phenomenon in the meniscus.

(iv) Important processing effects on solar cell efficiency have been demonstrated. These show the need for the presence of oxygen during the growth process in ribbon pulled from melt contained in graphite crucibles, combined with special thermal treatment sequences during the processing, in order to maximize cell efficiencies in this ribbon. With proper attention to these factors, small ($\sim 6 \text{ cm}^2$) cells of over 13% have been prepared from resistance-furnace cartridge-grown ribbon.

Several factors have prevented the technical features demonstration, with incorporation of the above developments into multiple 10 cm wide ribbon growth, from achieving required performance levels. Simultaneous growth of three 10 cm wide ribbons for periods of several hours has been demonstrated, but at

s) and duty rates well below those desired. Currently, s) cells made from this ribbon are in the 8% range. Unex- p) irregularities in the multiple furnace main zone and in- teraction between thermal fields in it and the cartridge, viz., die-top isotherms, are the main causes for reduced growth sta- bility that result in lower speeds and productivity. Seed rib- bon breakage has been an additional contributor to lower pro- ductivity. Work is being continued on finding tractable solu- tions to remedy these situations, as well as characterizing cartridge configurations that have produced ribbon at the de- sired speeds and with the necessary growth stability. With re- spect to the quality, the design changes needed to achieve con- trol over the growth ambient have not been implemented because of the continued state of development of the multiple furnace during preparation for technical features demonstrations. In summary, the differences between the individually demonstrated goals in single-cartridge growth and the multiple-ribbon fur- nace performance have well-defined origins, which are believed to be rooted in the inadequacy of the present design of the multiple ribbon furnace main zone configuration. The confi- dence that this shortfall and related program tardiness can be resolved simply by design iterations is consequently very high.

II. HIGH SPEED GROWTH AND QUALITY STUDIES by J.P. Kalejs

A. Overview

The development of a cartridge for growth of 10 cm wide ribbon at speeds of the order of 4 cm/minute and of a quality sufficient to give greater than 10% efficient solar cells has been given top priority in the operation of Furnaces 17 and 18 (JPL No. 1) in the past year. These speed and quality levels for 10 cm wide ribbon have been achieved in single cartridge furnaces. Studies have been continued to better understand factors influencing material quality in cartridge systems. The concentration of gases in the meniscus environment such as CO and CO₂, reactive with silicon melt, has been demonstrated to be a dominant factor in improving the efficiency of cells made on ribbon grown from graphite crucibles. Small area (~6 cm²) cells of 12 to 13% have been achieved on ribbon grown at low speeds (2 cm/minute) in cartridges without cold shoes. Implementation of ambient effects in high-speed systems has proved to be more difficult, although improvements in cell efficiencies to 10 to 11% have been demonstrated for ribbon grown at 3.5 cm/minute.

Computer modeling of heat and mass transport during ribbon growth has been undertaken in order to calculate interface shapes and impurity redistribution in the meniscus. The results have shown that the die top temperature is a primary variable affecting interface shape. Effects of die displacement and ribbon cooling profile on interface shape have been investigated, and the calculations have been extended to study transport of oxygen and carbon associated with meniscus-ambient interactions. Studies have been made on fast-cooled ribbon, utilizing the environment of the growth furnace. The

rate of cooling is observed to affect the SPV diffusion length, with this dependence also a function of ambient conditions.

B. Experimental

1. Machine 17

The development of the 10 cm cartridge system has proceeded in conjunction with work in Furnace 16 (JPL No. 3A). Quality and speed optimization studies have proceeded in parallel in Furnace 17, while the experiments in 16 have emphasized work on speed optimization and growth stability related problems. The progress made in the areas of speed optimization and quality is examined under separate headings below.

a. High Speed System Growth Characterization

Early trials with the 10 cm cartridge had shown that it was capable of growth of 10 cm wide ribbon with low levels of stress at speeds of the order of 4 cm/minute.⁽¹⁾ A further task undertaken was to achieve routine operation and reproducible growth conditions, and so define a baseline system with respect to which to conduct speed optimization studies. This was done by examining in detail factors that are operative in limiting growth stability and the maximum speed at which acceptable productivity levels may be maintained. Initially, minor redesign of some cartridge components and correction of deficiencies in power availability were found to be necessary to obtain a degree of die-top isotherm uniformity and reproducibility satisfactory for optimization studies. Growth conditions in the speed range from 3.5 to 4.0 cm/minute were generally excellent, with good long-term stability and control of ribbon width during seeding. Die design changes, with respect to capillary slot width and displacement, and cold shoe placement were not observed to significantly influence performance of the cartridge in this speed range. Although speeds as high

as 4.6 cm/minute were achieved, none of these changes had a well-defined impact on improving growth conditions above 4 cm/minute. In general, signs of increasing growth instability and a higher incidence of freezes were observed consistently in all attempts to increase growth speed above 4 cm/minute in the "baseline" cartridge.

Experiments in two other areas have been initiated to help to clarify the influence of additional factors on growth performance and speed capability of this baseline 10 cm cartridge. These involved growth with profiled cold shoes in Furnace 16 (as described in Section III) and comparison of growth performance with identical cartridges in Furnaces 16, 17 and 18. Profiling the cold shoes, by modifying their cross section to change the relative cooling capacity between the ribbon center and edges, has shown promise in preliminary tests in Furnace 16.⁽²⁾ The speed capability for acceptable operating conditions was increased to the range of 3.8 to 4.0 cm/minute from the previous range of 3.0 to 3.2 cm/minute. A cartridge from Furnace 16 with a profiled cold shoe has been tested in Furnace 17, and shows that improved growth conditions up to 4 cm/minute resulted from these changes. Additional tests are being carried out to study the growth performance above 4 cm/minute with profiled cold shoes, both in Furnaces 16 and 17.

Exchange of identical cartridges between furnaces has also revealed that a substantial influence on growth conditions is being exerted in the evolution of cartridge design by differences in the main zone configuration (heater and insulation package). In the course of experiments done over the early stages of development of the 10 cm cartridge in Furnaces 16 and 17, it was not recognized that these effects are much more important in the 10 cm systems than they were for the 5 cm systems. However, main zone and cartridge thermal profiling in Furnaces 16 and 17⁽³⁾ and experience with the 10 cm cartridge in Furnace 18 (see below) have shown the main zone heater and

insulation configuration have a significant influence on die-top isotherms and choice of operating conditions. As a consequence, the information gathered in optimization studies in the single-cartridge furnace has not always been found to be useful or applicable in improving growth conditions in the multiple furnace, and vice versa. Standardization of main zones and cartridge components has now been undertaken to reduce differences in design insofar as is possible in order to remove uncertainties in comparison of growth performance in future work.

b. High-Speed System Quality

Differences have been noted in the response of material properties to changes in meniscus gas composition between the so-called "low" and "high" speed cartridges; the cartridges differ by the absence or the presence of cold shoes, respectively. Introduction of CO and CO₂ into the meniscus environment has been shown to lead to significant improvements in properties of ribbon grown in a cartridge without cold shoes, at speeds of the order of 2 cm/minute.⁽¹⁾ Attempts have been made to improve material quality in the high-speed growth configuration with similar ambient manipulations. These have met with only limited success. Responses in material quality comparable to those observed in the low-speed system are very much in evidence when the cold shoe is introduced, but they are not consistently reproduced. Thus, run average SPV diffusion lengths in ribbon grown at about 4 cm/minute show increases to the range of 30 to 40 μm (from a baseline of 15 to 30 μm) when CO or CO₂ concentration levels are deliberately increased. Frequently, values in the 60 to 70 μm range are attained on individual 1 cm diameter barriers. However, growth conditions have not yet been defined that allow diffusion lengths greater than 40 μm to be reproducibly attained. Thus, they still lag the best results obtained in

growth without the cold shoes, as do the cell efficiencies, which have improved to give top efficiencies of 10 to 11%, rather than the range of 12 to 13% demonstrated for low-speed growth. Work in a number of areas has been initiated in order to gain a better understanding of the factors affecting ribbon quality in the high-speed as compared to the low-speed systems. This encompasses both experimental and theoretical studies, some of which are discussed in more detail in later sections.

Historically, unresolved differences in material quality have existed between ribbon grown in high-speed systems and that produced in MTSEC pilot production units, operating at 2 cm/minute. Since the latter are also induction rather than resistance heated, and differ further from the JPL furnaces by utilizing quartz instead of graphite crucibles, it has not been possible to ascribe differences in ribbon quality between these systems exclusively as originating from growth speed itself or from the cold shoe/afterheater arrangement peculiar to the high-speed system. This dilemma has been brought into sharper focus with the results from ribbon grown in cartridge systems with the cold shoes removed, and from studies of ambient gas composition effects on material quality in this system. It has subsequently become evident that the quality improvements achieved through ambient composition manipulation in the low-speed cartridge system, with a graphite crucible, have rendered this ribbon equivalent in most electronic characteristics to that grown from the induction-heated systems with quartz crucibles.

This recognition has been important in suggesting future research directions for quality studies in high-speed systems because it has provided additional insight as to how the cold shoe/afterheater and/or growth speed may contribute to producing the material property differences observed between high- and low-speed-grown ribbon. For example, as described in detail below, modeling of interface shape and ambient-meniscus

melt interactions has shown the extent to which growth speed may impact interface shape and impurity distributions, both by mediating the effectiveness of the ambient-meniscus interaction, and by altering the distribution of impurities originating in the bulk melt.

Directions for experimental work that have evolved from the present state of understanding include: (1) engineering of a more effective and more uniform means to introduce gas to the meniscus environment; (2) study of the relative importance of bulk melt oxygen, such as originates from use of quartz crucibles, and oxygen introduced via ambient meniscus interactions; (3) study of the effect of the post-growth thermal cooling cycle on material properties; and (4) investigation of the possibility that the cold shoe construction material contributes contaminants to the ribbon. Some of this work is already underway, as reported below.

2. Machine 18 (JPL No. 1)

The experimental effort on this furnace has been divided between studies of ambient effects in low-speed growth of 5 cm wide ribbon and conversion to growth of 10 cm wide ribbon. Additional investigation of the effects of introducing different ambient species into the meniscus environment has demonstrated CO_2 to be the most effective in improving cell efficiency. In cartridge growth without cold shoes, and with CO_2 present, cell efficiencies of 12 to 13% have been achieved. This improvement appears to be related to the introduction of oxygen into the ribbon. Mechanisms by which this may occur are discussed in Sections II-C and IV. In the case of the CO_2 -grown ribbon, interstitial oxygen levels increase to the range of 1 to 5×10^{17} atoms/cc. However, no correlation of oxygen concentration and cell performance has been found to date. SPV diffusion length increases and cell improvement are in evidence already before detectable IR in-

terstitial oxygen concentrations are reached (the detection threshold varies from 1 to 5×10^{16} atoms/cc, depending on the ribbon thickness). For the case of CO, oxygen is not detected even at the highest concentrations (~1000 ppm) for which acceptable growth conditions can be maintained. CO levels in the range from 50 to 500 ppm lead to the highest SPV diffusion lengths. An increase in the frequency of appearance of large grains also occurs in this concentration range, although no connection of quality to large-grain growth has been revealed by these experiments.

It was noted above (Section 1-b) that a means of ambient manipulation has not yet been implemented in growth with cold shoes that has improved cell efficiencies to the extent observed without the cold shoes present. The initial cold shoe runs were made in Furnace 18 with 5 cm wide ribbon, with reduced main zone conditions as well as with CO introduced to the cartridges. Since a number of components in the meniscus region were constructed of molybdenum, which is known to be easily oxidized, the use of CO₂ was postponed until the 10 cm cartridge became available in Furnace 17, as described above. Only occasional material improvement was achieved in high-speed growth in Furnace 18; more often, diffusion lengths decreased with increasing CO concentrations, and cell efficiencies did not improve over previous baseline values for the cold shoe system: 8 to 10%. The more positive responses obtained more recently with the 10 cm cartridge suggest that a factor such as the presence of the molybdenum could be responsible for the behavior seen with the 5 cm ribbon. The gas distribution system has also been changed in the 10 cm cartridge, and this improves the probability that the gas introduced to the cartridge reaches the meniscus region. Further work in this area is clearly needed, as it is not known how gas flow patterns may change with the addition of the cold shoes, or whether they may act as a sink for condensible

gases, such as SiO , and so alter the composition of the meniscus environment.

The task of converting Furnace 18 to 10 cm wide ribbon growth was started in the last quarter of this reporting period, but it has been hampered by several problems. A number of power supplies have not been capable of handling increased power demands, and it has been necessary to upgrade them. Initial trials of cartridges that had been used to successfully grow ribbon in Furnace 17 showed that growth conditions in Furnace 18 were much poorer. The growth difficulties were traced to differences in the main zone insulation, which had changed the die-top thermal field to such an extent that operating conditions could not be established with the end and face heaters in use. Modification of the main zone insulation resulted in acceptable growth conditions. However, due to limitations imposed by furnace design, an exact replication of the insulation packages in all the furnaces has not been feasible. This has complicated optimization studies, as already noted above. Additional standardization is planned to reduce differences in the furnaces to as great an extent as possible.

C. Material Quality Studies

The demonstrable influence of reactive gases in the meniscus environment on material properties has introduced a new direction for study of mass transport responsible for the ribbon impurity content and distribution. Since the reactive gases known to be present in the furnace (e.g., CO , SiO) contain carbon and oxygen, the balance of these elements in the ribbon will undoubtedly be affected by the strength of the ambient-meniscus interaction. Given the significant improvements observed in cell parameters with ambient manipulation, it must be concluded that these elements, either in combination with other impurities and defects or individually, have an important influence on material properties. With this in mind, studies of

impurity transport, particularly for carbon and oxygen, have been undertaken to help provide understanding of the basic processes that will govern their incorporation into the ribbon.

Foremost in formulation of an approach for transport studies has been the need to understand differences that may exist between growth with and without cold shoes; that is, between the high- and the low-speed systems. Implicit in this question is the role oxygen and carbon have in determining material quality, insofar as differences are observed in the response of ribbon properties to ambient manipulation in these two systems.

In the most general view, differences between the high- and low-speed systems that may contribute to the diverse behavior observed can be placed in four categories: (1) thermal, (2) speed, (3) metallic impurity, and (4) carbon-oxygen balance related. These categories may of course contain interactive phenomena, so the purpose of the division is to emphasize the origin of the processes that may affect the material quality. Thermal origins would include the effect of the post-growth furnace cooling schedule imposed by the cold shoe/afterheater combination, and effects that relate to the growth speed, which also sets the furnace (in situ) cooling rate. Aside from the cooling rate-related impact, growth speed will influence interface shape and the impurity distribution in the melt, and place kinetic restrictions on the effectiveness of the ambient-melt interaction. The distinction between metallic impurities and carbon and oxygen is important to make, since their effects on quality and their sources may differ. It is not known to what extent metallic impurities may be introduced by the cold shoe. Because of its close proximity to the interface and to high temperature regions of the ribbon, these impurities have easy access to the material if they enter the furnace gases either by sublimation from hot surfaces or as volatile oxides which result from surface oxidation.

The work that has been carried out to address some of the questions regarding differences between high- and low-speed

growth is discussed below. Analysis of transport phenomena has been started with the purpose of investigating the relationships between interface shape and melt impurity distributions that are characteristic of these two growth configurations. Another objective has been to compare the usual symmetric growth situation, that is, using a non-displaced die, to that existing with the displaced die. Finally, carbon and oxygen transport associated with ambient-meniscus melt interactions, which have resulted in improved ribbon quality, has been modeled. In other work, the relationship of furnace (in situ) cooling and ribbon quality has been investigated by fast-cooling or "quenching" ribbon immediately after growth.

1. Interface Shape

Computer modeling of the interface shape through the ribbon thickness has been undertaken in collaboration with Dr. L.-Y. Chin at Clarkson College. The finite element program developed at Clarkson appears to be unique in the field of crystal growth in that it is specifically designed to model interface shapes. In addition, the finite element aspect of the program allows more accurate representation of the meniscus and die contours that would be possible with a finite difference scheme, since the calculation domain elements can be chosen to be any arbitrary shape.

The domain of the calculation is a plane through the ribbon thickness, and the interface shape effects modeled are, therefore, those associated with temperature fields in this plane. A diagram of the calculation domain is shown in Figure 1. A two-dimensional, three-region model is constructed to calculate the temperature and flow field in the liquid, the solid temperature field, the die temperature field, and to include the phase boundary between liquid and solid. By employing the model to conduct a parametric study, the relationships between quantities such as thermal gradients and the interface

FIGURE 1
Geometry and coordinate system for calculation
domain in ribbon thickness dimension.

shape and position, which affect the crystal quality, and system parameters such as die design, crystal growth speed, and boundary conditions for heat transfer can be obtained. The governing equations of the model are applied separately to the liquid, to the solid, and to the die domain, with the appropriate boundary conditions for the field variables and one additional boundary condition for the interface position.

The parameters of die configuration are w_1 , w_2 , w_3 , w_4 , L_1 , and L_2 , as shown in Figure 1. w_1 , w_2 , w_3 , and L_1 are held constant at 0.025 cm, 0.15 cm, 0.005 cm, and 0.25 cm, respectively, for all calculations. L_2 and w_4 are adjustable variables for die design. When $L_2 = L_1$ and $w_4 = w_3$, the die is of the standard type and the domain is symmetrical about the y-axis. If L_2 is lower than L_1 , then the system is asymmetrical and models a displaced die. The effect of die geometry is investigated by comparing results for the symmetrical and the asymmetrical cases. The values of $L_2 = 0.2375$ cm and $w_4 = 0.01255$ cm are used for asymmetrical cases. The parameters in the governing equations and in the boundary conditions are v_g , T_{e1} , T_{e2} , T_b , T_{in} , y_s , T_t , and w . For all cases, the parameter y_s , which defines the calculation domain of solid region, is held constant with $L_3 = 0.5$ cm. The numerical constants given above correspond to a capillary channel dimension of 0.025 cm (5 mils), with a wider flat on the displaced side.

Because of the large number of variables in the complete matrix of parameters covered by the calculations, to specify them each time would confuse the discussion. Thus, when comparisons are made, only the variables compared will be named, and it is assumed other variables have standard values which are not of paramount importance in the discussion. Otherwise, independent variables used are the ribbon cooling profile on Γ_7 and Γ_8 (no cold shoe vs. cold shoe temperature distributions), ribbon thickness w , growth speed v_g , die top temperatures T_{e1} and T_{e2} , die base temperature T_b , melt inlet temper-

ature T_{in} , and die top location (symmetric vs. asymmetric or displaced die). More details of the calculation are available in an earlier report.⁽⁴⁾

Typical streamlines of the melt flow field are shown for the symmetric die in Figure 2. There is always a stagnant zone above the die top, and this likely promotes the growth of SiC particles, unless the meniscus surface were to be moving, such as could be the case if surface tension-driven flows were to be present.

In the temperature field specifications for interface position and shape calculation, the only "known" temperature input was assumed to be that of the ribbon cooling profile. Specifically, the two independent cases considered were the "slow" cooling and "fast" cooling profiles, inferred from measurements with ribbon thermocouples, without and with cold shoes in the 7.5 cm cartridge respectively. These are shown in Figure 3 for the first 0.5 cm above the die top. Calculations using curve (a) will be denoted by the term slow-speed system, (b) by high-speed system. All temperatures below the interface were investigated parametrically.

The interface shape was found to vary surprisingly little with most of the parameters investigated. Deviation of the interface from flatness also remained in a narrow range, in the order of 4 to 6% of the ribbon half width, over a rather broad range of input temperature profiles and growth speeds. The die top temperature emerged as the single most important controlling parameter for meniscus height. This is illustrated in Figure 4 for the symmetric die. It can be seen that a one-degree variation in the die tip temperatures, T_{e1} and T_{e2} ($T_{e1} = T_{e2}$), changes the meniscus height by about 20% in the range of growth velocities from 0.02 to 0.05 cm/second (0.5 to 1.25 inches/minute). On the other hand, doubling the velocity raises the meniscus height by about 33%. Changes in the melt inlet temperature, T_{in} , have virtually no effect; in going

FIGURE 2
Streamlines for flow field in symmetric die.

FIGURE 3
 Prescribed temperature distributions used in calculations for (a) low-speed, and (b) high-speed system.

FIGURE 4
 Dependence of meniscus height on crystal growth speed for
 two die top temperatures: (a) $T_{e1} = T_{e2} = T_m + 4$;
 (b) $T_{e1} = T_{e2} = T_m + 5$. Symmetric die and
 low-speed system cooling profile.

from $T_{in} = T_m + 50$ to $T_m + 150$, the meniscus height changes only by about 1%, with negligible change in curvature. Variation in the die base temperature T_b from $T_m + 25$ to $T_m + 100$ increases the meniscus height by about 30%, but does not change interface shape significantly.

With the understanding that the die-tip temperature is an important parameter in determining the interface position, calculations for the asymmetric or displaced die and for the comparison of low- and high-speed growth systems concentrated on this variable. The interface location for different values of T_{e2} with T_{e1} kept constant at $T_m + 5$ are shown in Figure 5 for the low-speed system. This illustrates the sensitivity of the interface tilt to T_{e2} for the asymmetric case. It is also interesting to observe that the interface will be nearly horizontal and close to the symmetric case for $T_{e2} = T_m + 8.5^\circ\text{C}$; thus, the benefits of the die displacement will be seen to be negated, when it comes to impurity redistribution, if the die tip temperatures happen to have such a temperature balance.

The case of higher speed growth of 0.06 cm/second (1.5 inches/minute) with the cooling profile appropriate to a cold shoe system and displaced die was examined as a function of die top temperature. The result for interface position and shape dependence on these parameters is qualitatively similar to that shown in Figure 5. With the change in cooling profile to the curve (b) shown in Figure 3, an increase in die tip temperature of about 5°C was needed to give a comparable meniscus height to that calculated with the low-speed profile (a). No significant variation of interface curvature with speed was found with the curvature remaining at about 5% of the ribbon half width at 0.06 cm/second (1.5 inches/minute).

The influence of ribbon thickness on interface shape was examined for the displaced die and the low-speed cooling profile. The interfaces for thicknesses of 0.020 cm (8 mils) and 0.030 (12 mils) are shown in Figure 6. In general, it is dif-

FIGURE 5
 Interface shape and position function f at $V_g = 0.02$ cm/second
 for asymmetric die (a) with $T_{e1} = T_m + 5$ and
 various values of T_{e2} compared to symmetric die (b)
 with $T_{e1} = T_{e2} = T_m + 5$; low-speed
 system cooling profile.

FIGURE 6
 Interface shape and position function f for two different ribbon thicknesses (a) $w = 0.02$ cm; (b) $w = 0.03$ cm. $V_g = 0.02$ cm/second with low-speed cooling profile.

difficult to parameterize the interface shape and position changes with variables such as thickness and cooling profile because they are in some measure interdependent. For example, for a given cooling capability (i.e., net heat flow out of the ribbon), in a real system the actual temperature profile in the ribbon is a function of ribbon thickness. This is illustrated in Figure 3. It is an effect often neglected. In measuring temperature profiles in a given system with ribbon thermocouples, for example, the ribbon thickness must then be specified. In the present case, if it is assumed the given initial profile (solid line) was for the 0.02 cm thick ribbon, then the profile for the 0.03 cm thick ribbon growing in the same system will be displaced upward by 10 to 15°C, as shown by the dashed line in Figure 3. Care must be exercised in the comparison of the two interfaces, as shown in Figure 6, in that the cooling profile is the constant factor here. More specifically, the two interfaces in Figure 6 are representative of ribbons grown in systems with different cooling capabilities.

2. Melt Mass Transport

In this section, mass transport and impurity distributions associated with some of the interface shapes discussed above are examined. The impurity distributions reflect temperature field influence on interface shape, melt flow influence on mass transport in the die top capillary and meniscus melt ahead of the growth interface, and impurity segregation at the interface. Aluminum and carbon were treated in detail. Aluminum is of interest because its diffusion coefficient in liquid silicon is known, and it has been used as an intentional dopant to test the model results. Carbon is present in concentrations generally far in excess of other impurities in the melt, and is likely to be a factor in producing structural changes and in governing the appearance of SiC.

The relationship between a given interface shape and impurity distribution is not a simple one. It is a function both of the segregation coefficient k_0 and of the melt diffusion coefficient D for the impurity, as well as of the melt velocity field characteristics near the interface. This is illustrated in Figure 7 for the representative impurities, aluminum and carbon. For both of these, k_0 and D have been measured and are known with reasonable confidence. The interface changes predicted produce the greatest variation in the carbon concentration profiles. Thus, for Figure 7(a), the ratio of carbon concentration in the ribbon on the high die side to that on the displaced side is calculated to be 4.7:1; for 7(c) the ratio is 1:3.8. For the case of 7(b), the carbon concentration in the ribbon center is about 50% higher than that at the ribbon surface. In contrast, these differences in aluminum concentration for the same interface shapes are much smaller, with variations in concentration of about 25% at the most. This is due to a higher value of D for aluminum, which ensures that diffusion dominates the impurity transport in the thickness dimension to a much greater extent, thus tending to smooth out concentration differences.

Several general relationships for impurity redistribution through the ribbon thickness and interface shape are worth noting. As illustrated in Figures 7(a) and 7(c), at large tilt angles θ the high side of the interface will always have the higher impurity level. The slope of the distribution and the difference in concentration levels between the two ribbon faces decreases with increasing D of the impurity. The interface tilt is also shown to be affected by the die top melt flow field, through the capillary exit geometry and ratio of the slot-to-ribbon thickness. This may lead to exceptions to the impurity distribution-interface slope relationship at low tilt angles. Distributions of the shape shown in Figure 7(b) would be typical of ribbon grown without die displacements or

FIGURE 7

Comparison of calculated ribbon concentration profiles for aluminum ($k_0 = 0.002$, $D = 5 \times 10^{-4} \text{ cm}^2/\text{second}$) and carbon ($k_0 = 0.07$, $D = 5 \times 10^{-5} \text{ cm}^2/\text{second}$) for three temperature field and interface configurations. C_0 is the incoming melt concentration and C_{Si} is the interface concentration for the impurity. θ is the tilt angle for the interface.

with small displacements. In this case, if interface breakdown were to occur, it would do so preferentially within the cross section of the ribbon, where the impurity concentration has its maximum. It is interesting to note that these maximum (central) concentration levels have not been found to exceed the average melt concentration (C_0) by more than about 25% for the growth configuration and impurity parameters investigated.

A die displacement that is capable of producing the impurity distribution of Figure 7(a) is clearly most desirable if cell junctions are to be made on the right-hand face of the ribbon. This also is preferable from the point of view of moving the impurity maximum of the form shown in Figure 7(b), which could lead to defects within the ribbon cross section, away from the good face. The point at which the transition from the general shape of Figure 7(b) to that in Figure 7(a) takes place is thus of interest. An optimum die displacement would ensure that the shapes in Figure 7(a) are achieved everywhere across the ribbon width.

Aluminum can be useful as a tracer dopant when the relation between interface shape and concentration profile is available, as in Figure 7. This is illustrated in Figure 8. Spreading resistance traces have been obtained on beveled, polished surfaces across the ribbon thickness for material grown with a displaced die (~0.008 cm displacement) from a melt deliberately doped with aluminum. The nominal doping level was 3.5 Ω -cm, and the resistivities measured on the ribbon were in the range of 3 to 9 Ω -cm, as shown, with aluminum the known majority carrier. Examination of the thickness traces shows the resistivity is about 20% higher on the average on the low die (displaced) side than on the high die side, indicating the latter has the highest aluminum concentrations. Comparisons of the measured traces with the profiles in Figure 7 allow one to conclude that the interface shape and temperature field during

FIGURE 8

Spreading resistance (resistivity) profiles for aluminum-doped melt taken through the ribbon thickness and along the growth direction on a $2^{\circ}52'$ bevel at six locations across the ribbon width. The displaced die side during growth was on the left hand side and the deduced interface shape as shown in the diagram above (note the displaced die side is on the opposite side from that drawn in Figure 7(a)).

growth was closest to that given in Figure 7(a).^{*} The angle $\theta = -16.8$ degrees for the interface slope means that the interface location (with respect to the horizontal) is 0.006 cm (~2 mils) lower above the displaced die side in comparison to that above the non-displaced side. The magnitude of change is about the order of the error in measurement of meniscus height with a microscope reticule, so this measurement has not provided direct confirmation of the interface tilt. However, in measurements made on Furnace 18, the difference in location of the interface position from one ribbon face to the other was indeed found to be small and of the order of the measurement error. The correspondence between available resistivity data and the model predictions is important to give confidence that the model can relate to real growth situations and is relevant to representing impurity redistribution phenomena that occur in practice during growth of EFG ribbon.

The presence of carbon has been associated with SiC growth at the die top and with the appearance of cross-sectional grain structure. Both of these phenomena occur asymmetrically with respect to the ribbon thickness dimension in growth from displaced dies, and are shown to correlate with asymmetries predicted for carbon concentration profiles obtained from the model results. For example, a carbon distribution corresponding to the interface shape of Figure 7(a) is confirmed to be most likely to occur in practice with displaced dies from comparison of calculated and experimental aluminum resistivity profiles, such as those given in Figure 8. The extra carbon in solution in the melt on the non-displaced die side thus can be expected to promote SiC growth there, and decrease the availability of the carbon on the opposite side, where the SiC deple-

^{*}A one-to-one correspondence is not sought because the die displacement used in experiments (0.008 cm) and that of the model (0.012 cm) do not allow it.

tion occurs. Figure 9 illustrates the correspondence between carbon distribution asymmetry and development of asymmetric cross-sectional structure in ribbon grown with displaced dies. Deviations from the usual parallel boundary structure, which typically may consist of linear dislocation arrays or short segments of grain boundaries aligned parallel to the ribbon surface, consistently occur nearer the ribbon face growing from above the non-displaced die flat (Figure 9(b)). In cases where a more complicated defect structure exists within the cross section, perhaps with an increase in the number of grain boundaries, none of which intersect the ribbon surface (Figure 9(c)), this again forms nearer this same ribbon face. At the same time, the discussion above has shown that interface shapes and carbon distributions somewhere between the extremes shown in Figures 7(a) and 7(b) are to be expected for growth with the displaced dies used in practice. The carbon distribution shown in Figure 9(a) is calculated for 0.03 cm thick ribbon, and shows the locations of the maximum in the carbon concentration and the cross-sectional defect structure exhibit the same asymmetry with respect to the die displacement.

The two impurities for which mass transport has been investigated here are representative of a large number of those of interest in silicon crystal growth. Impurities with $k_0 \geq 0.1$ will undergo relatively little redistribution regardless of the value of D . These include phosphorus, arsenic and boron. Carbon ($k_0 = 0.07$) and aluminum ($k_0 = 0.002$) are representative of impurities which have k_0 in the range from about 10^{-1} down to 10^{-4} (Cu, Ga, In, Sb, Sn). The known values of D for impurities fall in between those used in the calculations (Al has the highest known D). For comparable k_0 , a greater degree of redistribution can be expected with decreasing D over this range, thus increasing differences between the ribbon center and surface concentrations. The diffusion coefficients in liquid silicon for many impurities of interest be-

FIGURE 9

(a) Carbon distribution
in thick ribbon;
 $W = 0.03$ cm.

(b) Micrograph of ribbon
cross section. Low
die side is to the
right;
 $W = 0.026$ cm.

(c) Micrograph of ribbon
cross section. Low
die side is to the
right;
 $W = 0.040$ cm.

cause they are detrimental to ribbon quality are not known (Fe, Mo, Ti, Co, Ni). These impurities also have very low distribution coefficients ($k_0 \leq 10^{-5}$). Carbon can be considered to be representative of those which have low D, aluminum for high D, to obtain a qualitative estimate for the shape of possible redistribution profiles.

Oxygen is an impurity of special interest, but k_0 is not known with any certainty and D has not been measured. However, since the given values of k_0 in the literature range from 0.5 to 1.25, redistribution in the melt by the processes considered so far is minimal.

3. Ambient-Meniscus Melt Interaction

Most impurities are not transported across the meniscus surface. The bulk melt will be their main source, and the melt transport processes and distributions considered above should describe their distribution in the ribbon adequately (except for those for which solid-state diffusion after solidification is appreciable). This is not the case for oxygen, which is contained in gases that are shown to react strongly with silicon melt in certain situations. Carbon also is a special case in this respect, as reactions with die material are continuously affecting its melt concentration, while ambient gases may also account for some net transport through the meniscus. Such processes may therefore alter the distributions in the ribbon from those presented above. In the experiments which have shown that ambient compositional changes can significantly influence quality of ribbon grown in graphite crucibles, oxygen-bearing gases are used to produce the most interesting effect. Accordingly, the calculations have focused on the modeling of transport processes for oxygen.

In order to correctly represent possible physical processes and realistically model impurity transport, all the

sources and sinks of carbon as well as oxygen in the ribbon growth process have to be carefully considered. The calculation domain in the present case is restricted to the melt contained by the top of the die and the meniscus. The model thus can illustrate what happens to oxygen swept up the die by melt convection, then subjected to segregation and redistribution by convection and diffusion in the meniscus, and acted on by either sources or sinks at the meniscus surface.

Sources for oxygen at the meniscus surface are created when an oxygen-bearing reactive gas (such as CO or CO₂) is introduced into the meniscus environment. In addition, free oxygen will be present. This may be brought in by the argon purge gas, or arise as a by-product of CO₂ interaction with graphite furnace parts. There is some question as to whether SiO gas will be a source of oxygen, either as a by-product of reaction with graphite to form CO, or by dissolution in the silicon melt. The specific reactions that produce oxygen are unknown to the extent that any or all of these sources may be important in a given growth system. However, the appearance of interstitial oxygen in ribbon grown from graphite crucibles but with oxygen-bearing gases in the meniscus environment gives proof that transport processes in the meniscus melt are a significant source of oxygen in EFG ribbon given the appropriate ambient. Processes that generate oxygen flux out of silicon melt are also possible. Such sinks can be envisioned to result when carbon is available to form CO in the melt, and this is then evolved as a gas.)

A unique feature of the EFG system is that the growth interface melt (i.e., that in the meniscus at the die top) and the crucible (bulk) melt ambients can be made independent of one another in a way that is not possible in conventional CZ or float zoning. This possibility now increases the number of combinations of sources and sinks to be considered for oxygen to two: (i) The melt arriving at the die top may be low in

oxygen content if a graphite crucible is used, but then be exposed to an oxygen-rich ambient which introduces oxygen through the meniscus; (ii) Oxygen may be present in the crucible melt but then be evolved through the meniscus before solidification. The object of the calculations will be to predict the maximum oxygen transfer rates possible as a function of growth parameters (meniscus height, ribbon thickness, growth speed) in these two situations, and the resulting distribution through the ribbon thickness.

(1) Oxygen Source: The modeling has examined the effect of several parameters on the interface oxygen distribution for a source of strength unity imposed at the meniscus surface and with zero incoming oxygen concentration in the melt entering the die top and meniscus region. The results are presented in Table I by giving the average concentration in the ribbon and the maximum (surface) and minimum (center) concentrations. The calculated values are also dependent on the liquid silicon diffusion coefficient. This is taken to be $5 \times 10^{-5} \text{ cm}^2/\text{second}$, the same as that for carbon. This value is also the lowest that has been measured for any impurity in liquid silicon. A higher value of D would mean that more oxygen than that shown would get into the ribbon, and also that the difference between the maximum and minimum concentrations would decrease. In the calculations it is assumed that the concentration in the incoming melt is zero in all cases. Thus, the values given represent the maximum oxygen for the value of D that could diffuse into the meniscus, and get into the ribbon, in the time that the melt spends at the die top before solidification. The calculations also use $k_o = 1.25$.

The trends in average ribbon oxygen concentration illustrated by the tabulated results follow the expected trends for a diffusion-controlled process sensitive to the area of the oxygen source (meniscus surface) and time of residence of the

TABLE I
PREDICTED OXYGEN CONCENTRATIONS IN RIBBON AS A FUNCTION
OF GROWTH PARAMETERS. INCOMING DIE TOP MELT CONCENTRATION IS
ZERO; STRENGTH OF MENISCUS SOURCE IS UNITY.

GROWTH PARAMETERS				RIBBON OXYGEN CONCENTRATION		
Case	Thickness (cm)	Speed (cm/sec)	Meniscus Height† (cm) (average)	Average Ribbon Level	Maximum (Surface)*	Minimum (Center)
<u>Symmetric Die</u>						
SC-1	0.02	0.02	0.018	0.40	0.67	0.27
SC-2	0.02	0.03	0.021	0.32	0.66	0.17
SC-7	0.02	0.03	0.017	0.28	0.59	0.12
SC-8	0.02	0.04	0.020	0.24	0.61	0.08
SF-4	0.02	0.04	0.027	0.32	0.65	0.13
SF-5	0.01	0.04	0.027	0.56	0.70	0.50
<u>Asymmetric (Displaced) Die</u>						
AT-3	0.02	0.02	0.0194, 0.0204 (0.0200)	0.50	0.78 (0.76)	0.37
AT-10	0.02	0.02	0.0150, 0.0180 (0.0165)	0.42	0.61 (0.72)	0.30
AT-4	0.02	0.02	0.009 , 0.015 (0.0120)	0.38	0.77 (0.69)	0.21
AT-9	0.03	0.02	0.0186, 0.0204 (0.0195)	0.35	0.71 (0.75)	0.13
AT-11	0.02	0.06	0.0195, 0.0194 (0.0195)	0.17	0.52 (0.64)	~0.001

† The first value is for the non-displaced die side; the second is for the displaced side. The value in parentheses is the average height.

*The first value is for the non-displaced die surface; the number if parentheses is for the displaced side.

melt in the meniscus. Thus, the average level decreases with increasing growth speed, with increasing ribbon thickness, and with decreasing meniscus height. Extremes are illustrated by the thinnest (0.01 cm or 4 mil) ribbon grown at 0.04 cm/second (1 inch/minute) and a high meniscus, where a maximum of 56% of the oxygen concentration imposed at the ribbon surface can be introduced into the ribbon (case SF-5); also, at a growth speed of 0.06 cm/second (1.5 inches/minute) only 17% of the surface concentration will be introduced (case AT-11). It is evident that in order to get more oxygen than this into the ribbon at higher speeds, the ribbon must be grown thinner than 0.02 cm (8 mils) or with a higher meniscus. All things being equal, these calculations present a strong argument for growing with as high a meniscus as possible if the ambient is used as a means of introducing oxygen into the ribbon. In this area, the present design of cartridge system has very little flexibility. Meniscus heights are of the order of 0.015 to 0.030 cm (6 to 12 mils), in the range of those modeled. This is due to a relatively high h_{eff} which thins the ribbon before higher menisci are obtained.

IR spectrophotometry has shown that ribbon grown with CO_2 typically has interstitial oxygen concentrations in the range from 1 to 5×10^{17} atoms/cc for growth conditions approximately represented by cases SC-1 or AT-3 in Table I. The calculations thus show that an oxygen source as high as 1×10^{18} atoms/cc would be required to interact with the meniscus melt to produce the highest level observed. Other considerations make it clear that the ambient cannot be a source of more than about this level of oxygen given the growth parameters and value of D for oxygen. The foremost limitation arises because at a sufficiently high partial pressure of oxygen, spontaneous formation of SiO_2 will take place on the melt surface. Kaiser and Breslin⁽⁵⁾ have shown that this occurs at oxygen pressures of about 8 mm Hg (1.0×10^{-2} atmospheres or 10,000 ppm) and, subsequently,

that silicon melt solidified under this or higher partial pressures never contains more than about 2×10^{18} atoms/cc of interstitial oxygen. Evidence that in practical EFG ribbon growth with CO_2 oxygen source gases may be close to this level takes the form of the meniscus surface film cover that appears during seeding at the higher concentrations used (close to 10,000 ppm), when the melt is not in motion. This surface film probably is composed of SiO_2 and SiC . Eventually the levels of the deposits rise high enough to produce appreciable film formation which leads to deterioration of the die top thermal balance, with the appearance of clumps or clusters of deposits on the die top and patchy film on the ribbon. CO_2 levels at which this deterioration becomes severe are generally above 1000 to 2000 ppm; thus, there is qualitative agreement in this area between the phenomena observed in silicon ribbon growth with CO_2 and the experiments of Kaiser and Breslin; and also agreement in the level of interstitial oxygen in ribbon observed by IR and that predicted by the calculations on the assumption that oxygen source gas partial pressures in the meniscus ambient are capable of producing a meniscus source of the order of 1×10^{18} atoms/cc.

The distribution of oxygen found through the ribbon thickness, which has been calculated for several of the cases given in Table I, is illustrated in Figures 10 and 11. The ribbon center values at the lower speed are typically a factor of two to three below those at the surface. The profile shape is, of course, dependent on the value of the diffusion coefficient for oxygen in liquid silicon that is chosen for the calculation. As noted above, a value has been used that is thought to represent a lower bound, thus also representing minimum oxygen diffusion effects. The speed dependence of the oxygen distribution shown in Figure 10 is a central finding in the calculations, and has important implications in attempting to improve material quality in high-speed systems by ambient manipulation. It is seen that already at a speed of 0.06 cm/second, or 1.5 inches/

FIGURE 10
Comparison of the oxygen distribution at the growth interface at two different growth speeds with a meniscus source of unity.

FIGURE 11.
Oxygen distribution at the interface as
a function of ribbon thickness for a meniscus
source of unity. Growth speed 0.02 cm/second.

minute, the ribbon center oxygen concentration has dropped dramatically by several orders of magnitude from its value at 0.02 cm/second (0.5 inch/minute).

(ii) Oxygen Sinks: This situation can arise experimentally when the melt is rich in both carbon and oxygen, and the partial pressure of CO in the meniscus environment is below that for equilibrium with the meniscus melt carbon and oxygen. Evaporation or evolution of CO is then favored thermodynamically. Figure 12 shows the calculated oxygen profiles in the ribbon for one case. In the calculations, the melt entering the die top has a concentration of unity, and perfect sinks ($C = 0$) are placed on the meniscus surface. In this ideal situation, the calculations show that a maximum 60% of the original oxygen content of the incoming melt can be removed by evaporation. The trends with growth speed, ribbon thickness and meniscus height discussed above in the case of an oxygen source at the meniscus surface are then reversed: More oxygen than that shown in the example in Figure 12 will be removed with decreasing speed, decreasing ribbon thickness and increasing meniscus surface when the sinks are operative.

Experimental Observations: It is interesting to examine whether actual ambient conditions in practical EFG ribbon growth will promote evaporation of CO from the meniscus, or the reverse. For temperatures near the melting point of silicon, thermodynamic arguments⁽⁶⁾ show that a partial pressure of CO of 5.5×10^{-4} atmospheres or ~550 ppm is the saturation pressure for CO in contact with silicon melt containing carbon and oxygen. Experiments with SiC and SiO₂ saturated melts have shown that a saturation CO pressure of 3.8×10^{-4} atmospheres (~400 ppm) can be expected in this case.⁽⁷⁾ The carbon and oxygen levels in the melt in equilibrium with this CO level are about 4×10^{18} atoms/cc of oxygen and 1×10^{19} atoms/cc of car-

FIGURE 12
 Oxygen distribution at the interface
 with a perfect meniscus sink.
 Growth speed 0.02 cm/second.

bon. For CO levels below the equilibrium, oxygen can be removed from the melt given an appropriate source of carbon exists also. Above this pressure, a reaction of the CO with Si will be favored, with products SiC and SiO.

Given the fact that EFG melts have high carbon levels and high melt velocities are involved, it is not certain that the above equilibrium situations have any meaning in the EFG case. However, the formation of surface deposits on the bulk melt surface is observed quite frequently in addition to the meniscus film discussed above, and it can be speculated this occurs because the CO level exceeds some equilibrium value, although not necessarily corresponding to one of those given above. In Furnace 18, deposits on melt contained in graphite crucibles have been observed to occur always when the main zone purge rate is reduced sufficiently. The CO levels in the furnace are estimated to be of the order of 200 to 500 ppm when conditions favorable to deposits are reached.* This is within the range expected for the equilibrium pressure in the more ideal cases. On the other hand, all the interesting effects observed with increases in CO pressure — reduction of SiC particle density, onset of large-grain growth, and increase in as-grown material diffusion lengths — have also been documented to occur in the range of partial pressures of CO from 50 to 500 ppm. Thus, the experimental evidence strongly suggests that in EFG growth the equilibrium CO partial pressure, acting as a sort of dividing point between CO concentrations that activate processes which introduce oxygen into the melt (sources), and those that may allow oxygen to be evolved (sinks), has important bearing on material quality.

With high argon purge rates, CO levels in Furnace 18 drop to the range of 10 to 20 ppm. These pressures would then favor the process of removal of oxygen from the melt via CO evolution.

*These deposits are observed after cool-down, and may of course be formed during solidification.

These are the conditions under which the standard "graphite-like" material, with no detectable interstitial oxygen is produced. It has been observed in cartridge systems that a low level of CO can be maintained around the meniscus and film-free ribbon produced even with quartz crucibles by maintaining high argon purge rates in the cartridge, and thus not allowing SiO or CO generated in the main crucible melt to penetrate into the meniscus region. Interstitial oxygen levels have been below the detection limits in samples grown under these conditions. This result suggests that use of a quartz crucible is not a sufficient condition to ensure detectable interstitial oxygen levels in ribbon in these furnaces.

There are several important conclusions that follow from the modeling and these can act as a guide to research work in the crystal growth area in the future. The calculations show that the meniscus ambient must be considered as a first order factor in determining ribbon quality in two respects. First, it can act as a source of oxygen, which is particularly important for growth from graphite crucibles. However, it is capable of being a factor in growth from quartz crucibles for the same reason, particularly if crucible melt conditions are such that the oxygen level there is below 10^{17} atoms/cc. Second, the ambient can introduce impurities other than oxygen into ribbon. These will be distributed in much the same way as shown to be the case for oxygen if they are contained in gases reactive with silicon melt. Therefore, control of ambients must be recognized as essential if ribbon quality is to be optimized in EFG ribbon.

Some more specific effects that are important in considering quality improvements and understanding the ambient influence as a function of growth conditions are:

(a) Ambient effects in high-speed growth: The calculations clearly show that ribbon quality can suffer at higher growth speeds if the ambient is the primary source of

the oxygen that is required for quality improvement. This is a significant factor in considering system design. High meniscus growth and thin ribbon growth, preferably both, can be used to counteract this trend. Thus, there is an incentive to design systems with as low an h_{eff} as possible. At present, not enough data is available to say whether there is not another factor in the high-speed system that produces an additional first-order effect on quality (such as cooling profile or cold shoe contamination). Growth with quartz crucibles has not shown the expected improved cell performance. The reasons for this need to be understood.

(b) Ribbon thickness effects on quality: These can now be better understood. In a system where the crucible (bulk) melt has oxygen levels below the threshold needed for quality improvement, thick ribbon will have a lower average oxygen content for a given ambient than thin ribbon, although the near-surface concentrations will be comparable. These effects should be more pronounced the higher the growth speed, a situation which appears to be the case in practice. Again, quality will be less dependent on thickness in systems where the crucible oxygen content is high. Thus, we may not expect to see the same dependence of quality on thickness in quartz crucible-grown as we see in graphite crucible-grown ribbon.

4. Furnace Fast-Cooled Ribbon

The results of experiments on ribbon heat treatment, which utilizes the post-growth thermal environment of the growth furnace itself, are reported here. Changes in SPV diffusion length have been observed in ribbon fast-cooled in the afterheater temperature field which show that the rate of cooling of the ribbon in the furnace can significantly influence the diffusion length found in the as-grown ribbon at room temperature. Better understanding of these effects should provide

information to complement that obtained from heat treatment effects observed during processing.

The process of fast-cooling or "quenching" crystals grown from the melt long has been an important technique by which to help characterize material, e.g., the effect of cooling profile on defect generation.⁽⁸⁾ In conventional melt growth (CZ, float zoning), the cooling rates attained are dependent mainly on the surface-to-volume ratio of the crystal. Typical procedures, for example, achieve fast-cooling from 1412°C to 700°C in about one minute, with slower cooling thereafter.

The aspect ratio of the ribbon, width much greater than thickness, and a very high surface-to-volume ratio (proportional to the reciprocal of the thickness, i.e., typically ~50), leads to much greater and uniform cooling rates than associated with reported CZ or float-zone furnace fast-cooling experiments. Consequently, the rate at which the ribbon can be cooled depends only on how rapidly it can be removed from the furnace. In Furnace 18, a stroke puller with a maximum pull rate of 40 cm/minute is available. At this speed, the last-to-grow section of the ribbon, that next to the "quenched" interface, is out of the furnace in 30 seconds. The ribbon cools to less than 400°C in essentially the time necessary to remove it from the furnace. The average cooling rate thus is about 2000°C per minute or 33°C per second.

Typical results for SPV diffusion lengths measured on a strip barrier along the growth direction in a quenched sample are shown in Figure 13. The bottom curve represents a signal proportional to the diffusion length, while individual diffusion length measurements were taken at five locations with a reduced beam size, with the results as shown. The top curves give the furnace cooling profile and time that a given location on the ribbon has spent in the furnace cooling at the normal rate (set by the growth speed) before it is fast-cooled to room temperature from the location X, measured with respect to the

FIGURE 13

IR scan for fast-cooled sample (lower trace) and temperature-time relation for normal growth of 2 cm/minute (top graph). Results of individual SPV diffusion length measurements taken with a reduced beam size are given on lower graph. Results are for CO_2 ambient conditions. The last-to-freeze ribbon location is at $X = 0$.

die top. For example, the location (a) represents a portion of the ribbon that was grown out and cooled for 100 seconds at a rate determined by the normal growth speed while attaining a temperature of 1050°C , then was fast-cooled to room temperature in about 30 seconds. The SPV diffusion length measured on this section at room temperature was $34\text{ }\mu\text{m}$. Similarly, location (b) was cooled to 925°C in 200 seconds at the normal growth speed-related rate, then fast-cooled to room temperature in about 25 seconds. The diffusion length measured at room temperature was $46\text{ }\mu\text{m}$. The two dips in the lower continuous trace at 0.8 and 3.4 cm from the quenched interface arise from signal losses due to ribbon surface irregularities. Similar curves to that shown in Figure 13 have been obtained for ribbon grown under reduced main zone conditions and different speeds.

All the diffusion length traces for ribbon grown in the cartridge without the cold shoe show the same overall trends. Diffusion lengths are lower for the locations of the ribbon which are fast-cooled from temperatures above 800 to 900°C than for those locations fast-cooled from below 700 to 800°C . The distance from the interface (or temperature from which the fast-cooling takes place) at which the diffusion length increase occurs, shows some dependence on the ambient conditions as well as on the growth speed. The differences are difficult to quantify on the basis of the limited data, but it appears that the diffusion length increase for ribbon growth with CO_2 on generally takes place closer to the quenched interface than for the reduced main zone ambient. It can be stated more conclusively that any ribbon fast cooled from above 900 to 1000°C exhibits diffusion length values which are more typical of the baseline levels associated with standard gas flow conditions in Furnace 18 (i.e., values more typically representing levels achieved in low (less than 10 to 20 ppm) CO/CO_2 environments). The demonstrated ambient effects, with CO and CO_2 deliberately introduced to levels of a few hundred ppm or more, appear to

manifest themselves only if the ribbon is cooled at a rate corresponding to a normal growth speed of the order of 2 cm/minute to below at least 900°C. Thus, the benefits of the ambient effects could be perceived as not activated in fast-cooled ribbon when this cooling is initiated from above 900 to 1000°C.

Another feature that is observed in all traces taken on ribbon grown in the cartridge without the cold shoes is an increase in signal as the quenched interface location is approached. The diffusion length minimum in Figure 13 consequently occurs over a span of 2 to 4 cm from the quenched interface location. This ribbon location has already cooled through the steepest temperature drop at normal growth speeds over a time span of about 100 seconds, and is fast-cooled thereafter from temperatures of the order of 1100 to 1150°C.

Only one fast-cooled sample grown with the cold shoes at a speed of 3.8 cm/minute has been examined. The diffusion length in the fast-cooled portions remained low at all locations, and within the range of values observed in ribbon cooled at the normal growth speed-related rates. The ambient conditions were those associated with a reduced main zone purge rate (2 l/minute). Because of a lack of other data, it is not possible to say whether the difference between the diffusion length profiles of the cold shoe and no cold shoe ribbon is significant, or arises because of a non-recurring unknown factor in the case of this particular run.

The observed diffusion variations along a fast-cooled ribbon length as represented in Figure 13 may be viewed from two different perspectives:

1. The ribbon, when formed at the growth interface and at all subsequent lower temperatures reached by normal cooling, has a "good" diffusion length corresponding to values found in ribbon cooled to room temperature at normal rates, but the fast-cooling procedure itself destroys it.

2. As-grown ribbon is formed at 1412°C with a "poor" diffusion length in relation to its room temperature normal cooling cycle-related value, but the diffusion length can be improved if the ribbon is taken through an appropriate cooling cycle in the furnace, e.g., one associated with the normal growth speed-related cooling that takes place in a cartridge without a cold shoe. Hence, growth speed and/or in situ cooling rate and profile become a parameter in obtaining good diffusion lengths. Ambient conditions also appear as a factor in determining the temperature at which improvements are first realized.

At present, there is no evidence to favor either of these explanations, and work is continuing to further characterize the fast-cooled ribbon. In considering the first of the above possibilities, stresses induced by fast-cooling would at most lead to generation of dislocations as this stress is partially relieved in the cooling. These dislocations could increase recombination and decrease the diffusion length. Preliminary examination of fast-cooled ribbon cross sections has not revealed identifiable differences in ribbon structure as a function of distance from the quenched interface, and work is continuing in this area. As for scenario No. 2, several possibilities exist for explaining the results. For example, internal (i.e., bulk) gettering to improve diffusion length with time spent in the furnace could occur through association of impurities with local defects such as dislocations, boundaries, oxygen- or carbon-related complexes. Impurities would need to diffuse only short distances, of the order of the defect separation, to reach gettering sites. The surface is typically covered by a film of SiC/SiO_x , whose composition varies with the ambient composition. Surface film gettering will be most effective for fast-diffusion impurities, while it will not affect the bulk oxygen or carbon distribution. Effects arising from the presence of thermally-generated point defects (e.g.,

self-interstitials and vacancies) may also be a factor. A better understanding of the relation these processes have to material quality may be very important in understanding the differences that exist between low- and high-speed cartridge growth, particularly in the effect of ambient composition changes.

I would like to acknowledge the help of C. Radics in supplying the spreading resistance data, and J. Long for the cross-sectional and SPV data.

III. MULTIPLE GROWTH AND AUTOMATIC CONTROLS by B.H. Mackintosh

A. Overview

The one-year period covered by this report saw considerable progress in the consolidation and engineering development of the technology of growing 10 cm ribbon by EFG. The 10 cm cartridge came into existence four months prior to the start of this reporting period. By the time this reporting period began, the cartridge had been sufficiently refined that full-width ribbon had been grown on several occasions using the multiple ribbon furnace operating in a single cartridge mode.

In the last quarter of 1979, growth experiments were continued to improve the performance of the cartridge, and to further our understanding of the particular problems of growing and handling ribbon of this greater width. The additional equipment necessary to outfit Furnace 3A with three growth stations was also constructed.

In the first quarter of 1980, two multiple growth runs were performed to demonstrate the level of throughput performance of the 10 cm cartridge in a relatively early state of development. Following these experiments, a plan was established to systematically improve the performance of the overall multiple growth system to meet the technical features demonstration goals.

For the remainder of the first quarter, and all of the second quarter of the current year, the development work on the multiple ribbon furnace was concentrated in three areas, namely cartridge characterization, automatic controls development and cold shoe optimization. These efforts are described in later sections of this report.

Toward the end of the second quarter, several hours of simultaneous growth of two ribbons at 3 cm/minute was demonstrated, with one under fully automatic control. In another experiment, a cartridge was shown to be capable of sustained growth at 3.8 cm/minute with an improved set of cold shoes.

In the final quarter of this reporting period, the complete automatic control equipment for the second and third cartridge positions was installed on the furnace, all three cartridges were configured with cold shoes of the latest design, and three runs were made to attempt to demonstrate high-throughput multiple growth. Although in these runs the cartridge in furnace position No. 1, in which all development work of the past year has been done, operated very well, a severe and unexpected problem related to temperature irregularities in the main furnace prevented full-width growth from being achieved in furnace positions 2 and 3. These difficulties put in clear focus the fact that the 10 cm growth system requires a higher degree of optimization of those components affecting the temperature distribution in the die than was the case with the 5 cm cartridges. The relationship between the details of the temperature field in the main furnace and the die-top isotherm shape had not previously been closely studied. This relationship became a focus for development of the multiple furnace in the fourth quarter.

Two other problem areas stand out in the multiple 10 cm EFG technology in reviewing the cumulative experience to date; these, too, require concentrated development work before production-ready status will be attained. The first of these is thermal stress induced by the cooling profile built into the cartridge. This stress has continued, since the cartridge was first built, to manifest itself in frequent breakage of seed ribbons. The second problem is that the flows of gases within the multiple ribbon furnace are not sufficiently well defined or controlled to permit advantage

to be taken of the quality-enhancement techniques which have dramatically improved the photovoltaic performance of ribbon grown from the single-cartridge experimental furnaces over the past year.

B. Development of the 10 cm Cartridge

Over the course of the past year, the 10 cm cartridge has been refined in a number of ways. The most significant of these are discussed in the following paragraphs.

1. Die Top Radiation Shields

The cartridge was originally designed with a molybdenum die-top radiation shield as used in the 5 cm and 7.5 cm cartridges. To eliminate the molybdenum as a possible contamination source, a similar part made of graphite was first substituted, followed by a two-layered graphite radiation shield. The single graphite shield caused a significant decrease in attainable growth rate and loss of stability, due to the decreased shielding effectiveness of the higher-emissivity material. The two-layer design approximately restored the cartridge to the performance level achieved with the molybdenum shield, and, in addition, was thought to provide a potentially useful passage (between the shields) through which a gas stream may be directed at the meniscus. This technique is currently under investigation in Furnace 17.

2. Cold Shoes

During the initial six-month development period of the 10 cm cartridge, it became quite apparent that the cold shoes were not optimum with regard to their heat-removal function. The low growth rates attained, the difficulty in spreading the ribbon to full width, and the short duration of growth between freezes indicated an insufficient vertical gra-

dient in the edge regions of the ribbon. To correct this condition, various cold shoes were evaluated in which the vertical extent of the surfaces to which the ribbon radiates heat is greater near the ends than in the central portion. Details are given in Reference (2).

The long-term stability, controllability, and growth rate of an EFG system are largely determined by the combination of cold shoes, die top features, die heaters, and radiation shields. Three or more versions of each of these items have been experimentally tested. The current "standard" combination of these components which has evolved through this year's work is one which provides good short-term stability, i.e., low sensitivity to brief pull-rate and heating-power fluctuations, by the use of bulbous-ended dies to provide a relatively high meniscus at the ribbon end, and profiled cold shoes to create, in the thick ribbon end regions, a vertical gradient approximately as large as in the central portions of the ribbon's width. The optical automatic control equipment, described later in this report, imparts long-term stability to the overall system by maintaining the ribbon edges at fixed positions near the ends of the die.

An interesting feature of the profiled cold shoes is that the cartridge is unstable, with regard to ribbon edge position, when the edge is in the transition region between the thin and thick regions of the cold shoe. Upon entering this region while spreading, the ribbon edge will spread at an accelerating rate and a "freeze" will invariably occur unless the operator closely monitors the growth and increases power to the end-heater in appropriate stages. However, this instability is not a serious drawback; indeed it promotes the attainment of a full-width, end-bulb stabilized condition in a shorter time after startup than was typical in operation of the cartridge without the profiled cold shoes.

The particular version of the profiled cold shoes, which was installed in all cartridges during the recent multiple ribbon growth runs, was chosen simply because time did not permit the evaluation of other, thicker versions. We presume that thicker versions of this general configuration will display the same advantages over non-profiled shoes in providing growth rates somewhat above the current range of 3.3 to 3.8 cm/minute. The actual rate of growth of any cold shoe set depends on factors such as ribbon thickness, operator technique, and afterheater temperature setting. The tendency to produce buckled ribbon, which is characteristic of the cooling profile of the cartridge at present, may impose a practical limit on growth rate of slightly over 4 cm/minute, regardless of further cold shoe development.

3. Cartridge Characterization Measurements

In order to provide a general base of information to help in the interpretation of its behavior in growth experiments, and to support the further development of its various aspects, the standard cartridge existing at the end of 1979 was subjected to a series of temperature, power, and heat flow measurements. These measurements, made during the first quarter, have proven quite useful in diagnosing difficulties and guiding modification work. Details are given in Reference (3).

C. Automatic Controls Development

One of the most significant milestones in developing EFG into an industrial production process was reached in the past year with the demonstration of a practical, optically-based system for precisely controlling ribbon width. The background work on the use of a standard television camera, outfitted

with a special "anamorphic optics" system, as a sensor for geometric features of the growth meniscus was performed in 1978 and early 1979. The work of the past year has consisted of the following steps:

(i) The video analysis circuitry which derives D.C. control signals from the output of the TV camera was designed, fully tested, and packaged into a form suitable for this particular control task.

(ii) Additional circuitry was designed to interface the control signals from the video analysis unit to the existing temperature control equipment on the furnace.

(iii) The control system was utilized in an initial series of ribbon growth runs, during which its general behavior was observed and various measurements were made. The operator experimented with the control system to evaluate its usefulness during growth startups and in spreading ribbon to full width.

(iv) Following this initial period of experimentation, several modifications were made to the control electronics to make the system more convenient to set up and use.

(v) After successful trial of these modifications (item (iv)), the control system was duplicated to outfit the remaining two growth stations of the multiple furnace.

The complete automatic width-control system consists of the elements shown in Figure 14. The equipment includes all circuitry necessary to control the positions of both ribbon edges and the height of the meniscus near the die center. However, only the edge-position control loops have been utilized to date. In virtually all ribbon growth work so far, the edge-control loops have been configured for a proportional gain of about 3% end-heater power per 0.01 cm deviation of the ribbon edges. This gain results in stable control of the ribbon edge at any position within the region of effectiveness of

Automatic Ribbon Growth Control System

FIGURE 14

the end heaters (about 0.8 cm), provided that the pull rate and face-heater temperature settings are within acceptable ranges.

Although time has not yet permitted much analysis or development of the control system's performance, the apparatus has already clearly demonstrated its effectiveness in maintaining ribbon growth for over three hours on several occasions. There is no known mechanism in this system which should systematically limit the duration of unattended growth periods to only a few hours, and, indeed, most of the segments of steady-state growth in recent runs with the automatic controls have ended in "freezes" occurring with no warning. The causes of loss of control will be studied in greater depth in the near future.

Considerable attention has been paid to designing the automatic control equipment so that the operations of setting it up and closing the control loops at the appropriate times are as convenient as possible. The procedures required of the operator to establish growth under automatic control now consist of the following steps:

- (i) Ensure that the "anamorphicized" image of the die top is roughly centered in the video monitor by adjusting a small mirror.

- (ii) Adjust the vertical positions of the "ribbon-edge" video analysis windows on the monitor to be just above the top surface of the die.

- (iii) Initiate growth by manually controlling pull rate, face heater, and end heater controls. The ribbon will probably be growing at less than full width when the starting transient has ended.

- (iv) Move the video analysis windows horizontally to encompass the edges of the ribbon and momentarily switch the monitor to the "quantized" image of the growing ribbon.

(v) Adjust the "quantization level" pots on the video analysis unit to obtain a clear black/white image of each ribbon edge.

(vi) At any subsequent time, either edge of the ribbon may be placed on closed loop control by operating a toggle switch located next to the end-heater manual control pot. At the time the control loop is closed, the circuitry automatically defines the position occupied by the ribbon edge within the video analysis window as the reference input or control point, and will maintain it there until the control loop is opened by turning the toggle switch off. The operator may choose to spread the ribbon to full width by shifting the video analysis windows by small increments with the control loops closed, or may choose to manage spreading of the ribbon manually, and, once the edges are in the correct locations near the die ends, "capture" them there by closing the control loops.

Although the furnace was outfitted with three of these control systems during the last three runs of this period, there has not yet been a demonstration of fully-automatic multiple ribbon growth, for reasons discussed below.

D. Multiple Growth Runs

The seven multiple growth runs carried out during the reporting period are briefly summarized by Tables II and III. A significant feature of the data of Table III is that the throughput performance of the best functioning cartridge, generally that in furnace position No. 1, improved in discrete steps corresponding to the changes listed in Table II. Starting with run 230, the combination of profiled cold shoes and automatic width control system operated in such a manner as to yield nearly 100% full-width ribbon from cartridge No. 1. The high time percentages of these runs during which this station was operating represent the fact that ribbon growth was con-

TABLE II
MULTIPLE 10 CM GROWTH RUNS
OF FEBRUARY 1980 THROUGH SEPTEMBER 1980

Run No.	State of Development
215, 216 (February)	First multiple 10 cm operation. Cartridges with non-profiled cold shoes.
230, 231 (June)	Cartridges with profiled cold shoes ("3.0 cm/minute" version). Automatic end control on station No. 1 only.
241, 242, 243 (August/September)	Cartridges with profiled cold shoes (3.5 cm/minute" version). Automatic controls on all three stations.

TABLE III

THROUGHPUT DATA FOR MULTIPLE 10 CM
GROWTH RUNS OF FEBRUARY 1980 THROUGH SEPTEMBER 1980

Run No. →		215	216	230	231	241	242	243
Overall System:	Run duration (minutes)	572	360	208	90	390	300	295
	Total length grown (meters)	23.4*	22.6	22.8	Note 2	Note 2	9.1*	Note 2
	Time percentage of simultaneous three-ribbon growth	12.7	8.0	0	0	0	0	0
Cartridge No. 1:	Length grown (meters)	6.6	4.4	6.3	3.1	12.8	4.9*	9.4
	Percentage full-width ribbon produced	56	54	100	98	94	98*	90
	Percent of run time operating	38.6	40.8	100	100	96	48*	93.2
	Average growth rate (cm/minute)	3.00	2.99	3.03	3.05	3.40	3.4*	3.40
Cartridge No. 2:	Length grown (meters)	6.0*	4.4	Note 1	Note 2	Note 2	1.8*	Note 2
	Percentage full width	28	0	0	0	0	0	0
	Percent of run time operating	35.1	38.9				19*	
	Average growth rate	3.0*	3.18				3.2*	
Cartridge No. 3:	Length grown (meters)	10.8	2.7	5.5	Note 2	Note 2	2.4*	Note 2
	Percentage full width	65	14	96	0	0	0	
	Percent of run time operating	73.2	25.6	95.6			25*	
	Average growth rate	2.56	2.95	2.76			3.2*	

Notes: 1) Cartridge No. 2 was inoperable due to an assembly error.

2) Due to the large number of ribbon breakage incidents and unsuccessful startups, no meaningful throughput data were generated for Cartridges 2 and 3 in these runs.

* Estimated data.

tinuous over long periods, typically 1.5 to 3+ hours, with little or no operator attention. The operator's efforts during runs 231 through 243 were primarily directed toward achieving growth in the other two stations of the furnace.

The increase in growth rate between 230/231 and 241/242/243 was due to the different cold shoes utilized.

These attempts to operate the overall system at its full throughput capacity have thus far failed primarily due to two causes, as follows:

1. Distortion of Die-Top Isotherm Shape

Full-width growth could not be established in cartridges 2 and 3 in several of these runs because excessive and irregular temperature variations existed along the length of the dies. These variations resulted in the impossibility of growing ribbon simultaneously to both ends of the die (lateral imbalance) and in excessive thickness variations, including reduction to zero thickness in some cases during growth ("hot spots"). A cartridge in which ribbon cannot be grown to full width requires constant operator attention to sustain growth at all, and will nevertheless exhibit frequent freezes. In other cases, die top temperature variations may not be so severe as to prevent full-width growth but may cause ribbon to be grown with nonuniform thickness across the width, which increases the likelihood that it will fracture as it is being grown out. This is a manifestation of the same thermally-induced stresses which cause great difficulties with seed ribbons as discussed in (2) below. Figures 15 through 18 are photographs and diagrams of anamorphicized TV images of growth menisci which illustrate the difficulties encountered. Figure 15 is of a properly-shaped meniscus in steady-state growth. Figure 16 shows the images of two cartridges with distorted meniscus shapes which render full-width growth impossible. Figure 17 shows the extreme variations in profile of the stationary meniscus which

FIGURE 15
Furnace position No. 1,
run 243 (see text).

FIGURE 16
Furnace positions 2 and 3,
run 242 (see text).

FIGURE 17
Furnace position No. 3,
run 243 (see text).

FIGURE 18
Furnace position No. 3,
run 243 (see text).

result from the combination of a distorted isotherm shape and the nonuniform thickness profile of the ribbon previously grown from the die having that distorted isotherm shape. In Figure 18, the meniscus detaches at the hot center of this same die shortly after growth startup. In this instance, growth can only be re-established by the time-consuming process of inserting a new seed ribbon. Our current understanding of the underlying cause of these difficulties can best be explained by reviewing certain aspects of the design and development of this system.

A basic premise of the design of the multiple EFG ribbon growth furnace has always been that the temperature distribution within the die top is determined by the die heaters and other cartridge components, so that the details of the thermal field of the furnace in which the cartridge is operated do not need to be too carefully optimized. This premise was borne out in our experience with multiple 5 cm ribbon growth. Certain previous hot zone and heating elements used during the period of 5 cm cartridge development were unsatisfactory insofar as the melting temperature of silicon was not attained along the full length of the furnace. Once this gross condition was corrected, satisfactory growth of 5 cm wide ribbon was obtained at all five positions along the length of the furnace. The heating element configuration which was satisfactory for multiple 5 cm operation was retained when the furnace was modified to accept three 10 cm cartridges.

The longitudinal temperature profile of the furnace has been measured at various times by the technique of installing a graphite bar ("dummy load") in place of the crucible, plugging the cartridge openings, and inserting a thermocouple into wells drilled in the dummy load at the center and edges of the cartridge positions. Profiles obtained in this way for different sets of heating elements which vary slightly in dimensional detail and in resistance are shown in Figure 19. Experience has

FIGURE 19
Furnace 3A temperature profile measurements for various heating element combinations taken by "dummy load" method.

shown that certain deviations from "flatness" are desirable in these profiles to compensate for "end effects." Specifically, the cartridge in furnace position No. 1 is flanked on the left by the melt replenishment unit which runs hotter than the cartridge to its right, in position No. 2. The cartridge in position No. 3 "sees" the unheated end region of the furnace to its right. Thus, in both these positions there is a lateral temperature imbalance which requires compensation through the design of the main heating elements or some other means. The aspect of the main furnace temperature profiles which remains poorly defined at present is the influence of the local details, i.e., the temperatures of the individual segments of the multi-slotted heating elements, upon the temperature distribution in the dies.

This difficulty did not come to light until recently because all single-cartridge development work since the introduction of the 10 cm system was done in furnace position 1, where, somewhat fortuitously, the die-top isotherm has been generally satisfactory (e.g., Figure 15). Also, it must be pointed out that in runs 215, 230, and 241, two of the three cartridges as well as significant portions of the control electronics were newly assembled. In effect, each of these was a "shakedown run," where component misfits and control problems could not be ruled out as causes of the observed difficulties. It was only after the cartridges were carefully inspected and interchanged among furnace positions following runs 241 and 242 that the irregular meniscus profiles were clearly identified as features of furnaces positions 2 and 3 rather than of the cartridges.

The remedy for this situation, which we will now carry out will be to look more closely at the temperature distribution of the hot zone, and define more precisely the ideal distribution for this layout in which there are three growth stations with the melt feeder at one end. Because we are antici-

pating the construction, in the near future, of an improved version of this furnace which will have a different arrangement of growth stations in the hot zone, it is essential that a better methodology for refining hot zone temperature profiles be developed.

2. Ribbon Breakage Due to Thermal Stresses

In the Annual Report for the period ending in September 1979, one of the outstanding problems mentioned in regard to early development of the 10 cm cartridge was the breakage of seed ribbons. The statement made on this subject may be paraphrased as follows:

"Seed ribbons frequently break when inserted into the cartridge due to the abrupt transition between room temperature and about 550°C occurring at the entrance to the linear cooling plates. The problem is currently severe but will probably be alleviated when an adequate supply of full-width ribbon, grown with uniform thickness across the width, carefully cut and handled to avoid mechanical damage, has become available for use as seed ribbons."

Although the careful selection and handling of seed ribbons has proven essential to successful growth of 10 cm ribbons, the seed breakage problem has continued to plague us, causing severe loss of growth time, degradation of cartridge performance (due to broken ribbon pieces melting on the die) and contamination of the system (via the methods used to retrieve broken pieces of ribbon from within the cartridges). The cause of this problem has been well understood for the past year, and the likely remedy appears to be straightforward. However, the necessary redesign work has been postponed during this period for two principal reasons. The first is that the development of the cartridge for better stability and higher growth rate, as well as the implementation of automatic growth controls have been tasks of higher priority in meeting the technical features demonstration goals which were to be met by

the end of July 1980. The second reason for postponement of this partial redesign is that we have been awaiting guidance from the experimental work of Furnace 17 on additional cartridge design modifications which would permit the "oxygen enrichment" phenomenon to be exploited in the multiple ribbon furnace. The cartridge could then be improved in these two important respects in one "semi-major" redesign exercise.

E. Multiple Ribbon Growth Technical Features Demonstration Goals

The above paragraphs define the problem areas toward which work will be directed in the coming quarter. We expect that the die top temperature profile problems can be effectively solved, permitting multiple growth at about 3.5 cm/minute with duty rates approaching those required of production processes.

The achievement of average solar cell efficiencies in excess of 10% from multiple cartridge runs, however, does not appear likely by the end of this year, although the capability of single-station furnaces to produce ribbon surpassing this level has been clearly demonstrated.

F. Multiple Growth Furnace Production Prototype Model 3B

The design of this improved successor to the existing Furnace 3A, which was to have formally begun after successful completion of the technical features demonstration goals, is currently in postponement.

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IV. CELL AND MATERIALS CHARACTERIZATION

A. Cell Characterization by C.T. Ho

1. Overview

The study of the ambient effect on the photovoltaic property of the ribbon has been continued during the course of the experiments carried out in Machine No. 1. Evaluation of the solar cell output parameters and the bulk diffusion length enhancement characteristics leads us to believe that the oxygen impurity contained in the carbon saturated ribbon plays an important role in regard to the cell conversion efficiency.

It also has become clear that the thermal conditions in cell fabrication have a significant influence on the property of the processed cells. A proper selection of the diffusion processes used at MTSEC can yield a favorable cell performance depending on the ribbon growth parameters. For example, the CVD diffusion process is appropriate for ribbon grown from the standard graphite crucible with Ar purging ambient, while the PH_3 diffusion process is a better choice for the oxygenated ribbons grown under the CO_2 ambient conditions. In fact, the task goal for the fabrication of a 13% conversion efficiency small area (4 cm^2) solar cell has been successfully demonstrated with the latter procedures.

In the 10 cm wide, high-speed growth Machine 17, a baseline for the run average solar cell conversion efficiency has been established at 9 to 10%. Initial experiments with the CO_2 ambient gas have also shown evidence for the improvement of solar cell output to above 10%.

A multiple growth run, 16-216, with three cartridges growing 10 cm wide ribbon simultaneously has produced large

area ($\approx 55 \text{ cm}^2$) solar cells with an average conversion efficiency of 8%.

2. The Experimental Growth Furnace No. 1

The solar cell data for the ribbon grown from the various experiments during the reporting period are summarized in Table IV. The results can be discussed as follows:

a. High-Efficiency, Small Area Cell

Two cell fabrication runs were made in order to demonstrate the feasibility of achieving a conversion efficiency of 13% from resistance-heated (RH) furnace-grown ribbon. Samples were selected from baseline runs, 18-133, 18-150, reduced ambient run, 18-185, and CO_2 ambient run, 18-172. These samples have as-grown SPV diffusion length values ranging from 35 to 45 μm . The cell blanks were cut into $2.5 \times 5.5 \text{ cm}^2$, and processed into solar cells by both PH_3 (900°C diffusion with subsequent gettering) and CVD (1050°C diffusion from doped oxide source) junction formation processes. The BSF was formed by alloying the evaporated aluminum and the AR coating was sputtered Si_xN_4 film. The contact metal covered about 8% of the whole cell area.

In the PH_3 -processed run, HE-2, there exist several cells which have conversion efficiencies in excess of 12% (see Table V). Further reduction in the cell size for a few selected cells resulted in a cell of 5.8 cm^2 , with a conversion efficiency of 13.2%. Thus, we have demonstrated that a 13% conversion efficiency is attainable for RH-EFG ribbons.

b. Reduced Ambient Experiment

It has been previously pointed out⁽⁹⁾ that the photovoltaic properties of the grown ribbons could be influenced by the thermal treatment during the cell fabrication. We began

TABLE IV
SUMMARY OF AVERAGED SOLAR CELL DATA FOR RIBBONS
GROWN FROM EXPERIMENTAL FURNACE NO. 1
ELH LIGHT, 100 mW/cm², 28°C

Run No.	Growth Conditions	Process	Cell Parameter				Notes
			J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	
HE-1 (mixed lot)	reduced MZ	CVD	27.0	.57	.72	11.1	AR; 14 cm ²
HE-2 (18-172)	CO ₂ ambient	PH ₃	28.2	.58	.729	11.9	AR; 14 cm ²
18-170	CO ₂ ambient	CVD	24.1	.555	.711	9.5	AR; 55 cm ²
18-171	standard Ar purge	CVD	24.2	.549	.692	9.2	AR; 55 cm ²
18-172	CO ₂ ambient	{ PH ₃ CVD	19.1 18.5	.552 .546	.69 .73	7.3 7.3	no AR; 14 cm ²
18-173	CO ambient	CVD	23.7	.553	.695	9.12	AR; 55 cm ²
18-174	CO ₂ { off on	CVD	17.1 17.4	.536 .539	.704 .702	6.45 6.54	no AR; 55 cm ²
18-175	CO ambient	{ PH ₃ CVD	17.2 18.1	.532 .544	.73 .71	6.7 7.0	no AR; 14 cm ²
18-186	reduced MZ	{ PH ₃ CVD	17.2 18.3	.517 .542	.72 .75	6.4 7.4	no AR; 14 cm ²
18-188	reduced MZ	{ PH ₃ CVD	19.4 18.9	.545 .545	.70 .70	7.4 7.2	no AR; 14 cm ²
18-191	CO ₂ { off on	PH ₃	22.4 26.5	.509 .549	.73 .74	8.32 10.8	AR; 14 cm ²
	CO ₂ { off on	CVD	25.1 25.1	.548 .548	.74 .74	10.2 10.2	AR; 14 cm ²
18-199	CO ₂ { off on	PH ₃	21.1 26.7	.517 .565	.737 .703	8.04 10.6	AR; 14 cm ²
	CO ₂ { off on	CVD	26.5 26.6	.559 .557	.692 .687	10.3 10.2	AR; 14 cm ²
18-205	CO ₂ { off on	PH ₃	21.7 24.4	.527 .533	.738 .687	8.44 8.93	AR; 14 cm ²

TABLE V

SOLAR CELL DATA FOR RUN HE-2

ELH LIGHT, 100 mW/cm², 28°C; AR COATED

Cell No.	Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Notes
HE-2-1	14.3	28.5	.578	.701	11.6	13 cm ² ribbon blanks
-2	14.4	28.6	.578	.707	11.7	
-3	14.8	28.1	.579	.744	12.1	
-4	14.2	28.0	.581	.722	11.8	
-5	14.1	28.3	.579	.747	12.2	
-6	14.1	28.5	.581	.742	12.3	
-7	14.1	27.4	.574	.702	11.1	
-9	8.1	27.9	.581	.769	12.5	
HE-2-1A	5.8	29.0	.581	.764	12.9	scribing off edges
-1B	5.8	29.1	.581	.779	13.2	
-3A	3.8	28.3	.575	.769	12.5	
-7A	6.0	27.6	.575	.751	11.9	
-7B	6.2	27.9	.573	.773	12.4	
-9	7.1	27.7	.578	.783	12.5	

to adopt the two junction formation processes as an evaluation procedure to study the cell property. The initial investigation was applied to two reduced ambient-grown ribbons from runs 18-186 and 18-188.

As shown in Table IV, the PH_3 -diffused cells have lower output than the CVD-diffused cells in run 18-186, while the reverse is true for run 18-188. The lower output in 18-186 mainly manifests itself in both J_{sc} and V_{oc} , but in run 18-188 the higher output of the cell mainly originates from the higher J_{sc} . As we examined the bulk diffusion length, L_n , enhancement characteristics (Figure 20), we noticed the distinctive contrast between these two groups of cells. In the PH_3 -processed cell group, both ribbon materials show enhancements of L_n as the illumination level increases. But the lower output ribbon run, 18-186, shows, in general, more than 100% reduction in the magnitude of L_n from run 18-188 at all intensity levels. In the CVD-diffused group, none of the ribbon material shows enhancement in L_n , but the cell from run 18-186 shows only 30% lower than the higher output cell group, run 18-188. In addition, at the highest measurement illumination intensity level (10 mW/cm^2 of $1 \mu\text{m}$ light), L_n of the 18-188 cell group from the PH_3 diffusion has the tendency to surpass the corresponding CVD-diffused cell group. For the 18-186 cell group, this will not happen unless a much higher illumination level is reached.

From both the photovoltaic parameters and the diffusion length enhancement characteristics, we classify the solar cell behavior of group 18-186 as "graphite-like" and group 18-188 as "quartz-like." The connotations are derived from the previous experimental observations for material grown respectively from graphite crucibles and quartz crucibles in the RF furnace system. The actual role of oxygen impurity in relation to these classes of photovoltaic characteristics will emerge in the following CO_2 ambient gas experiment.

FIGURE 20

The classification of "quartz-like" and "graphite-like" photovoltaic behavior according to the bulk diffusion length enhancement characteristics. Cell samples were chosen from the reduced ambient growth runs 18-186 and 18-188.

c. CO₂ Gas Ambient Experiment

Growth run 18-191 has been made with the CO₂ ambient gas turned "on" and "off" during the growth process. The portion of the ribbon grown with CO₂ turned "on" has been found to contain a concentration of 4 to 6 x 10¹⁷ cm⁻³ interstitial oxygen in the material, and less than 5 x 10¹⁶ cm⁻³ (detection limit of the IR spectrophotometer) in the portion with CO₂ turned "off." Again, we separated the ribbon into two groups according to these ambient conditions, and proceeded to examine the photovoltaic characteristics of the solar cell by using the two diffusion processes.

From the output data for the cells, and the corresponding bulk diffusion length enhancement characteristics, we observe the equivalence of the "quartz-like" photovoltaic behavior in the "CO₂-on" cell group and the "graphite-like" behavior in the "CO₂-off" cell group. These results clearly show the consequences produced by the introduction of oxygen into the ribbon via CO₂ ambient gas control. A repeat run, 18-199, produced nearly the same results.

Thus, we can conclude that: (i) The quartz-like behavior of the solar cell is oxygen-related; (ii) The PH₃ diffusion with gettering is the preferable process for an oxygen-containing RH ribbon; and (iii) The CO₂ growth process is shown to give reproducible results with respect to the solar cell characteristics.

3. The High-Speed Growth Furnace No. 17

a. Baseline Runs

Several standard Ar flow growth runs have been made in the 10 cm wide, high-speed growth System 17 in order to establish a baseline ribbon quality. Solar cells were fabricated by the CVD process for runs 17-062 through 17-082.

As shown in Table VI, the baseline cell efficiency for the material grown from the graphite crucible system without intentional gas addition has been established to be 9 to 10% at a growth speed of 3.5 to 3.8 cm/minute.

b. CO₂ Gas Ambient Run

Ribbons from runs 17-084 to 17-107 were grown with the CO₂ ambient gas mixing with the main zone Ar flow. After the split-batch of PH₃ and CVD processing, the solar cell showed predominantly the graphite-like behavior. It is probable that the CO₂ gas has not been effectively transported into the silicon melt. Run 17-107 is an exceptional case, in which the PH₃-processed cell group resulted in a better cell parameter than the CVD-processed group. The bulk diffusion length enhancement characteristics again supported this quartz-like behavior. Thus, the improvement of photovoltaic output via CO₂ ambient growth has also been demonstrated in this growth run. However, further improvement in the gas introduction system is required before the CO₂ ambient gas can be fully incorporated as an integral part of the growth process in the furnace.

4. Multiple Growth System 3A

Run 16-216 was a multiple growth run which produced ribbon simultaneously from three 10 cm cartridges in the furnace system. The ribbons grown from each cartridge were separated and fabricated into 10 cm x 5.5 cm solar cells by the standard CVD diffusion process. Cell performance results under AM1 simulation measurement are summarized in Table VII.

Ribbons grown from cartridges 1 and 2 produced nearly the same averaged conversion efficiency, $\approx 8\%$, with the highest efficiency being 8.7%. Ribbons grown from cartridge 3 showed slight reductions in the output. The photovoltaic parameters

TABLE VI
SUMMARY OF AVERAGED SOLAR CELL DATA FOR RIBBONS
GROWN FROM HIGH-SPEED SYSTEM NO. 17
ELH LIGHT, 100 mW/cm², 28°C

Run No.	Growth Conditions	Process	Cell Parameter				Notes
			J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	
17-062	standard Ar purge	CVD	24.5	.547	.665	8.9	AR; 25 cm ²
17-072	"	"	23.2	.539	.73	9.13	AR; 55 cm ²
17-074	"	"	23.3	.542	.726	9.18	"
17-076	"	"	22.8	.541	.63	7.8	"
17-078	"	"	24.5	.546	.705	9.42	"
17-079	"	"	24.5	.543	.688	9.16	"
17-081	"	"	24.8	.547	.703	9.54	"
17-086	CO ₂ ambient	{ PH ₃	24.2	.541	.682	8.92	"
		{ CVD	25.6	.553	.683	9.64	
17-087	"	"	22.2	.518	.663	7.62	"
			25.0	.548	.662	9.0	
17-101	"	PH ₃	27.2	.565	.682	10.5	AR; 14 cm ²
17-107	"	{ PH ₃	26.0	.487	.717	8.43	AR; 55 cm ²
		{ CVD	24.0	.482	.625	7.22	

TABLE VII

SUMMARY OF SOLAR CELL DATA
FOR MULTIPLE GROWTH RUN 16-216.
THE CELLS WERE ALL CVD PROCESSED
WITH AREA 50 TO 56 CM²

100 mW/cm²; ELH LIGHT, 28°C; AR COATED

Growth Cartridge	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)
No. 1	21.8	.529	.661	7.6
	21.3	.525	.683	7.6
	22.4	.540	.721	8.7
	22.0	.531	.688	8.0
	24.4	.537	.609	8.0
No. 2	24.1	.533	.669	8.6
	24.4	.528	.666	8.6
	22.5	.522	.637	7.5
	22.4	.524	.619	7.3
	23.9	.531	.666	8.5
	23.3	.529	.671	8.3
No. 3	21.0	.515	.707	7.7
	21.0	.515	.629	6.8
	20.9	.515	.660	7.1
	21.6	.517	.684	7.6
	22.2	.522	.678	7.9

for all the cells in this run appear to be limited by the bulk diffusion lengths, which were found to be 12 μm in the typical samples.

B. Materials Characterization by J.F. Long

1. Overview

The format of this section represents a departure from past practice. Because the goals of each of the three furnaces have overlapped more regularly as progress toward the ultimate goals of the contract has been made, it was felt that a more cogent presentation of the material quality data could be made if this section were subdivided by topic rather than by furnace.

2. Detailed Description of Results

a. Standard 10 cm Wide Growth

During this past year, a large number of runs were conducted on Furnaces 16 and 17 to establish a baseline for 10 cm growth conditions and material quality levels. Tables VIII and IX summarize the results as well as the various difficulties encountered. This first series of runs in Furnace 17 established that average minority carrier diffusion lengths of 15 to 30 μm are achievable under standard ambient conditions (Table VIII). Within that series of runs, several (17-063 through 17-067) experienced systematic ribbon thickness gradients which resulted from cold shoe positioning problems. These runs were found to exhibit correlation between ribbon thickness and diffusion length (e.g., run 17-064, Figure 21). During this same series of runs, the transition from flat to displaced dies was made.

Due to the continued developmental nature of experiments in the multiple Furnace 16 (JPL No. 3A), a reduced number of quality evaluations were carried out. These are summarized in

TABLE VIII
SPV DIFFUSION LENGTH DATA FOR 10 CM WIDE
RIBBON GROWN IN FURNACE 17.

Run No.	Displaced Die	$\bar{L}_D$ (μm)	Comments
17-062	no	24.5	No cold shoe
-063	no	15.5	Thickness gradient side to side
-064	no	30.3	" " " " "
-065	no	28.5	" " " " "
-066	no	18.3	" " " " "
-067	yes	10.4	" " " " "
-068	no	20.5	Thickness gradient corrected
-069	yes	17.5	
-071	yes	22.8	
-072	yes	30.1	
-074	yes	27.8	
-075	yes	19.3	
-076	no	24.2	

TABLE IX

SPV DIFFUSION LENGTH DATA FOR 10 CM WIDE
RIBBON GROWN IN FURNACE 16 (JPL NO. 3A).

Run and Sample No.	Single/Multiple Cartridge	Auto Controls	$\bar{\rho}_-$ (Ω -cm)	$\bar{L}_D$ (μ m)
16-215-1	multiple	no	-	17.5
-2			-	29.1
-3			-	20.8
-216-1	multiple	no	1.4	25.1
-227-3B	single	yes	1.3	22.4
-3E			1.3	22.8
-3F			1.2	20.9
-3H			1.7	26.2
-3J			1.2	21.1
-3L			1.3	21.2
-228-4C	single	yes	0.9	25.0
-4D			0.9	19.8
-4E			0.9	20.6
-4F			1.3	18.6
-4G			1.5	20.0
-4H			1.3	19.8
-230-1-1A	multiple	cart. No. 1	1.0	27.8
-1-1G			1.0	29.6
-3-1D			0.7	18.8
-3-1G			0.9	21.5
-242-1-4B	multiple	cart. No. 1	-	32.4
-1-5A			8.8	16.6
-2-1C			11.9	10.5
-3-2C			6.1	7.5

FIGURE 21
SPV diffusion length (L_D) vs.
ribbon thickness (t) for run 17-064.

Table IX. In most cases, the diffusion lengths achieved equal past performance levels and compare favorably with the values established in the baseline runs in Furnace 17 shown in Table VIII.

b. Gas Ambient Studies

All three furnaces participated to some extent in this program, with the bulk of the work being performed in Furnace No. 1 (18) during 5 cm wide growth runs. These experiments have included reduction of main zone argon purge rates (with a concomitant increase in furnace CO concentrations), and introduction of various gases into the meniscus region. These results have been described in earlier reports.⁽¹⁾ Interstitial oxygen concentrations have also been measured in the ribbon by low-temperature infrared spectroscopy. The detection limit for $[O_i]$ for the typical EFG ribbon thicknesses is on the order of $5 \times 10^{16}/\text{cm}^3$ with this technique.

The study of oxygen-related phenomena has also been started for 10 cm wide ribbon in Furnace 17. Table X summarizes some of the results. These runs all grew 10 cm wide ribbon, with a cartridge gas delivery system quite different from that used in Furnace 18. The introduction of gases did not consistently lead to improved diffusion lengths. Also, interstitial oxygen was found only occasionally, and then in only trace amounts ($\sim 10^{16}$ atoms/cc).

Finally, Furnace No. 3A (16) undertook two runs involving manipulation of the ambient. The following table contains the pertinent information for run 16-217, which was a single-cartridge run involving manipulation of the furnaces argon purge rate as well as the growth speed. Significant improvement in L_D was observed at the reduced main zone purge rate. This improvement appears not to be hampered by the elevated growth speed. Sample 16-217-6 achieved the highest sample average L_D (average of nine measurements) seen to date on material from Furnace 3A.

TABLE X
SPV DIFFUSION LENGTH DATA FOR 10 CM WIDE
RIBBON GROWN IN FURNACE 17 WITH AMBIENT MANIPULATION

Run and Sample No.	Cartridge Gas; Flow Rate	$\bar{L}_D$ (μm)
17-084-1A	Ar; 1 ℓ/min	32.1
-1B	1% CO ₂ in Ar; 1 ℓ/min	31.7
-1E	1% CO ₂ in Ar; 0.5 ℓ/min	33.2
17-085-1A	Ar; 1 ℓ/min	32.9
-1B	1% CO ₂ in Ar; 0.5 ℓ/min	28.4
-1D	1% CO ₂ in Ar; 1 ℓ/min	34.1
17-098-1A	None	16.3
-1B	1% CO ₂ in Ar; 0.5 ℓ/min	27.2
-1C	1% CO ₂ in Ar; 1.0 ℓ/min	27.2
-1D	1% CO ₂ in Ar; 2.0 ℓ/min	29.9
17-099-1A	1% CO ₂ in Ar; 1.0 ℓ/min	37.0
-1C	1% CO ₂ in Ar; 3.0 ℓ/min	43.6
17-100-1A	1% CO ₂ in Ar; 2.5 ℓ/min	26.4
-1B	1% CO ₂ in Ar; 2.5 ℓ/min	38.0
17-101-1A	Ar; 0.5 ℓ/min	19.5
-2B	1% CO ₂ in Ar; 1 ℓ/min	29.7
17-111-2A	1% CO ₂ in Ar; 1 ℓ/min	20.6
17-112-1A	1% CO ₂ in Ar; 0.5 ℓ/min	35.5
17-114-1A	Ar; 1 ℓ/min	11.5
-1B	1% CO ₂ in Ar; 0.75 ℓ/min	22.5

Sample No.	Furnace Argon Purge Rate (ℓ /minute)	Growth Speed (cm/minute)	$\overline{L}_D$ (μm)
16-217-1	23.6	2.8	17.1
-2	16.0	3.3	17.2
-3	12.7	3.8	26.9
-4	9.4	3.2	19.3
-5	4.7	3.6	29.7
-6	4.7	3.8	40.3

Only one attempt was made to introduce CO_2 into the furnace ambient in Furnace 16. The gas was introduced as 1% CO_2 in argon as the main furnace purge gas. Flow rates from 1.45 to 2.0 ℓ /minute were attempted. No significant effect on the introduction of the CO_2 was observed ($\overline{L}_D = 20.2 \mu\text{m}$, CO_2 -off; $\overline{L}_D = 21.5 \mu\text{m}$, CO_2 -on).

c. Growth Speed Effects

The majority of these runs were performed on Furnace 17. Results from all three furnaces are contained in Table XI. All runs except 18-181 and 18-198 were 10 cm wide growth runs. Run 17-086 was the only run conducted without a cold shoe (hence, the low growth speed). It is clear that use of the cold shoe in Furnace 18 resulted in much lower SPV diffusion lengths than reported previously for growth without cold shoes.⁽³⁾ The reasons for this are not known. Diffusion lengths in Furnace 17 growth with the cold shoes were generally higher, but have not yet attained the best levels achieved in 5 cm wide ribbon growth without cold shoes.⁽¹⁾ Experiments to better understand the effects of the cold shoes and/or growth speed in combination with ambient changes on quality are continuing, as described in Section II.

TABLE XI

SPV DIFFUSION LENGTH DATA FOR SELECTED
HIGHER SPEED GROWTH OF 10 CM WIDE RIBBON

Furnace, Run, and Sample No.	Growth Speed (cm/minute)	$\bar{L}_D$ (μm)
17-078-1C	3.0	24.8
-1D	3.5	19.5
-079-2B	3.5	25.6
-2C	3.5	27.2
-080-1B	3.1	21.4
-1C	3.5	20.0
-081-1B	3.7	26.2
-1C	4.0	25.5
-082-2C	3.5	12.9
-2D	3.8	15.0
-083-1B	4.2	20.9
-1C	4.0	26.3
-086-1A	1.8	39.0
-1B	1.8	38.2
-087-2A	3.8	33.8
-2C	4.0	31.9
-088-1A	1.9	31.9
-2A	3.8	33.1
-089-1B	3.0	25.9
-090-2A	3.7	36.4
-091-2A	3.7	20.9
-092-1B	3.9	29.9
-093-1C	3.9	37.8
-096-1B	3.7	24.6
-097-2B	3.7	35.3
-102-1C	3.5	27.8
-103-1B	3.7	27.0
-104-1C	3.8	22.5

TABLE XI continued.

Furnace, Run, and Sample No.	Growth Speed (cm/minute)	$\bar{L}_D$ (μm)
-106-1C	3.8	36.6
-108-1A	3.0	34.2
-109-1B	3.8	23.8
-110-1C	3.9	27.5
-115-1C	3.8	25.4
-116-1B	3.8	23.2
-117-1B	3.8	32.6
-118-1B	3.5	16.8
18-181-1I	3.4	17.9
-2L	3.4	18.1
-3B	3.6	21.8
-3N	3.6	11.6
-4L	3.4	13.7
-198-1J	3.7	6.8
-2K	3.9	12.0
-3K	3.6	13.3
-4K	3.6	15.6
-219-1	3.0	22.5
16-234-4A	3.8	28.4
-4F	3.8	25.6
-4K	3.8	24.5
-5D	3.4	26.4
-5E	3.4	18.1
-235-1A	3.8	20.4
-3A	3.6	13.1
-4B	3.3	12.9
-4D	3.3	15.8
-5A	3.6	10.4

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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 83,769 and cost plus fixed fee was \$2,976,510. Man hours for fiscal year 1980 were 22,116 and cost plus fixed fee was \$885,556. Therefore, total cumulative man hours and cost plus fixed fee were 105,885 and \$3,862,066, respectively.

3. Engineering Drawings and Sketches Generated During the Reporting Period

See Section III, Figure 14, for details of automatic width control system.

4. Summary of Characterization Data Generated During the Reporting Period

See Section IV.

5. Action Items Required by JPL

None.

6. New Technology

The effort on the "automatic controls system," reported in Section III, has generated several items of new technology which have been separately reported. Some other items of potentially new technology have been, or will be, also separately reported pending possible patent action.