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LARGE AREA SILICON SHEET BY EFG

First Quarterly Report, January 1, 1977—March 31, 1977

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March 15, 1977

Work Performed Under Contract No. NAS-7-100-954355

Mobil Tyco Solar Energy Corporation
Waltham, Massachusetts

MASTER

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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ABSTRACT

During the quarter on which this document reports, the contract was modified by adding several new tasks.

They are: Work on an existing multiple growth furnace(Machine No. 16 now JPL No. 3A, designed and built in-house previous to the start of the contract extension at Mobil Tyco's expense) with the aim of achieving growth of 5, 2" wide ribbons simultaneously at a rate of 3 in./min. The report describes the equipment and the initial experiments carried out under this contract. Also starting is a task aiming to bring the 5 ribbons under automatic control, equally using pre-existing equipment and designs made at Mobil Tyco's expense.

Furthermore, the effort to characterize the EFG materials produced is increased and particular emphasis is placed on measuring and analyzing their solar cell performance. The report presents data on defect densities in various EFG grown ribbons, demonstrates that the diffusion length is larger under AM1 than under "dark" conditions, and shows results on electrical inhomogeneities in the ribbon cells. Many of these results are interpreted in terms of defect-impurity interactions which are believed to be the main impediment to better solar cell performance at the present time. However, data is reported on an EFG solar cell of 12% AM1 efficiency, and on several 1" x 4" EFG cells of efficiencies between 9 and 11%.

In the single ribbon resistance heated crystal growth station (JPL No. 1), which was already operating in the initial program before it was modified, a major effort is made to identify the sources of impurities introduced during growth by testing a variety of machine components and designs. Also work is being started to evaluate how 3" wide ribbons with low grown-in stress may be produced at rates of up to 3 in./min. These efforts are described in some detail.

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I. INTRODUCTION

The present program is part of a total Mobil Tyco Solar Energy Corporation objective to produce silicon ribbon for solar cells at a cost which will allow their wide scale use for generation of electric power. On February 14, 1977, it was significantly expanded with the addition of several new tasks. In order to carry out these tasks, major pieces of equipment which have been designed and built under in-house funded programs were made available for use under the contract, namely a multiple EFG ribbon growth station and automatic growth control devices.

The edge-defined, film-fed growth process itself was initially developed for the commercial production of continuous, shaped single crystals of sapphire from the melt and was applied to growth of silicon for solar cells partly under NSF Grant GI37067X via Harvard University, JPL Contract 953365, and under NSF Grant GI433873. The basic feasibility of the application of EFG to the growth of silicon ribbon has been proven and the theoretical base for extending the technique to the efficient production of single crystal silicon sheet has been established. There are three fundamental objectives which are now being pursued:

1. Demonstrate that from an improved, resistance heated EFG crystal growth station (JPL No. 1) it is possible to obtain growth of single, continuous ribbons, 3 inches wide at a rate of 3" per minute. These ribbons furthermore are to be of a quality sufficient for fabrication of solar cells between 8% and 12% AM1 efficiency.

2. Demonstrate, by using the resistance heated multiple growth station made available to the program by Mobil Tyco (Machine No. 16, now JPL No. 3A) that it is possible to grow simultaneously 5 ribbons of 2" width at 3"/min, using automatic control systems which have been developed also by Mobil Tyco and which are likewise made available to the program to be mated with the growth station.

3. Characterize the material grown not only in terms of its electrical and crystallographic properties, but more particularly as a solar cell. The aim here is to identify any fundamental barrier which might prevent the material from achieving 12% AM1 solar conversion efficiency when grown from the crystal growth stations employed here.

In summary the program is now entering into a greater engineering research and development effort. Thus, the crystal growth machines now being used can be considered forerunners of true production machines because of their capability for wide (2" - 3") high speed (3"/min.) multiple (5 ribbons) growth under automatic control. Also, with respect to the capability of the material to produce solar cells, the question is no longer whether EFG material is fundamentally capable of yielding solar cells of more than 10% AM1 efficiency, but, rather whether crystal growth machines operating at the high speeds required for economic reasons and with the complexity necessary for multiple growth can be designed such that they produce material from which large (e.g., 3" x 3") cells of good efficiency can be fabricated at high yields.

II. WORK ON CRYSTAL GROWTH STATION JPL No. 1

A. Crystal Growth Efforts

1. Experimental

During this reporting period, three Si ribbon growth runs were made. The purposes for Run No. 18-12 were to improve the standard handling/cleaning procedure and to evaluate the influence of various cartridge gas flows on ribbon purity. All Mo components were etched in 50% HF 50% H₂O to remove oxides, rinsed with H₂O, electrolytically etched in pure H₂SO₄ to remove surface films, rinsed with H₂O, and finally rinsed in pure methanol. All graphite components were baked out in a halogen atmosphere. The furnace was wiped clean then washed with ethyl alcohol until a white rag wasn't stained. After assembly, the furnace was vacuum baked to remove surface contaminants, etc. Total bakeout was about 5 hours, ultimate vacuum was 60 μ at temperature.

Six ribbons were grown. Ribbons 18-12-1 through 18-12-4 were grown under normal conditions: e.g., argon plus helium was fed into the cartridge to increase heat transfer from the growing ribbon to the cooling blocks. Ribbon -5 was grown with only argon fed into the cartridge and -6 with only the furnace ambient in the cartridge - no positive gas pressure in the growth region. Cartridge misalignment and a lower zone instability plagued all six efforts. 5 and 6 grew more slowly than 1 - 4, but were otherwise in all ways similar. There was no difference in the appearance of the ribbon from each growth.

Run No. 18-13 was a 'standard' growth effort, to retrain a 'rusty' operator. Four ribbons were pulled yielding ~12' of 2" wide material.

The purpose for crystal growth run no. 18-14 was to evaluate the comprehensive new clean procedures formulated during this period and to evaluate the effectiveness of a crucible cover. In preparation for the run, the entire crystal growth

system including the cartridge was disassembled, all the parts were thoroughly cleaned and the furnace was reassembled using a procedure designed to avoid contamination during assembly. To permit a thorough purging of the system and all the surfaces of the cartridge, a solid split charge was used and the cartridge was lowered into the growth position prior to argon purge. Thus the cartridge was in place during heat-up.

Shortly after a melt was achieved, an O-ring seal in the top of the cartridge failed and the run was prematurely aborted. When the station was disassembled the crucible holder and main heating element were found to have cracked. No other damage was incurred by the introduction of water into the system.

The crucible cover was thoroughly warped. This was due to the reaction of the bottom surface of the crucible cover with the SiO vapors above the melt forming silicon carbide in situ. Distortion results as the reaction takes place because the silicon carbide occupies more volume than the graphite from which it is formed. (The phenomenon has been observed before in closed crucibles.) This distortion is of relatively small importance in this series of experiments but must be overcome before the 'no-cartridge' experiments (in which the die is supported by the cover) are run. Possible solutions to the problem include the slotting of the bottom surface of the cover to allow expansion of the surface without distortion, the use of a footed crucible cover to allow escape of the SiO from the volume over the melt, the use of quartz or grafoil crucible covers, or, finally, the use of a graphite crucible to avoid the formation of SiO in the first place. These alternatives will all be evaluated during March.

Growth efforts in JPL 1 have been terminated prematurely due to power stud failure, cartridge component misalignment, and now, a water leak. Other component failures observed during the operation of this system include windows cracking, thermocouple failure, and heat shield package warping and collapse. Each of these modes of system failure has been relatively straightforward to diagnose and correct. Although the amount of downtime which has recently been experienced in this machine may be considered high, overall design has to be considered a success, because it is simple to operate and it produced ribbon almost immediately after it was built, which has not been true for all such designs.

The 3" cartridge designed for this system is, if anything, simpler than the current 2" cartridge and as easy to operate. It is reasonable to expect yield from this cartridge to increase by more than a factor of 2.

A longer range solution to the problem of SiO evolution is to reduce the ratio of melt volume to SiO₂ contact area. This may be accomplished by using shorter crucibles filled with molten silicon to greater depths. A 4" long quartz crucible (vs. 6" in use today) and suitable crucible holder will be designed and built for JPL 1.

Part of our new thorough cleaning process includes the removal of the heating element and power studs. The heating element is Ultra Carbon UT-6 graphite and the power studs are molybdenum. Approximately 1 out of each 2 times the system is disassembled and reassembled, 1 power stud is damaged on reheating. This is apparently due to poor contact between the molybdenum and the graphite; improvement has been realized by regrinding the tops of the power studs each time they are removed from the system and by removal of grafoil compression pads between the stud tops and heating element. However, a newly designed power stud/heating element contact will replace the present design. (Figure 1). In this new system the contact area between the molybdenum and the graphite increases by more than a factor of 3 and should thus reduce hot spot erosion.

2. Planning

Work on this machine is, of course, one of the ongoing tasks; and, as mentioned above, it is still in the process of being rebuilt to rectify various defects which we believe negatively influenced the ribbon quality or impeded the reliable operation of the growth station.

At present then, we are working towards a specific experimental program of 48 working days to determine whether indeed our approaches to higher purity are valid.

Prior to initiating the experimental series we have implemented several changes in the furnace which should generally help to keep it cleaner.

To avoid back streaming of pump oil we are installing a liquid nitrogen trap in the roughing pump line. To prevent contamination from the oil vapor mist, the roughing pump will be vented far from the growth system. Argon and helium lines have been sampled and the gases are being analyzed. Materials will include ultra high purity quartz for crucibles, quartz wool for the cartridges, graphite for crucibles, etc.

Concurrent with the first series of runs, reticulated vitreous carbon and fiber-form are being ordered for an all carbon shield pack system, quotes will be also sought for a tungsten shield pack and the molybdenum power studs have been

Fig. 1. Power stud and heating element with increased contact.

redesigned.

The experimental series starts with an all clean system and a covered crucible. This cover will isolate the source of detrimental impurities either inside or outside of the closed crucible holder. The crucible will be covered because, in past runs oxide deposits in the system have been observed to fall into the melt. The oxide deposits have been analyzed and found to contain many impurities including iron. The second growth run will see only limited system components replaced, e.g., the die, cartridge bottom plate, melt, crucible, crucible holder, crucible cover, and top shield pack. For Run No. 3 and Run No. 4 of the first experimental series, only these same parts will be replaced. Diffusion lengths on the material produced will be measured immediately. If the results of analysis of the ribbons from the first two runs indicate a substantial improvement in quality (e.g., diffusion lengths 15 - 20 microns) over all the runs to date, then the series will be completed to look for diffusion length and cell efficiency degradation, and repeated to validate the data. Assuming that the 8 run series is completed, sound purity information about the potential for products from the 2 inch cartridge will have been generated, the importance of a crucible cover will have been demonstrated, and the degradation of cell properties as a function of limited system cleanup will be clear.

At the end of 2 or 8 runs (depending upon the initial diffusion length measurements) a no-cartridge series of runs, Nos. 9, 10, 11, will be made. The purpose of this experiment is primarily to characterize the cartridge as a source of impurities, and also to look at the effects of growth rate. The system designed for no-cartridge experiments can be run with or without a one-piece top heater (and may take several additional trial runs to achieve stable growth and runs to produce enough material to answer the questions for which the experiment was designed).

The third series of experiments will be grown from the 3" cartridge (bringing this cartridge on line may take more than 3 runs). The new cartridge will change the growth environment in two ways. First, the cold shoe should be substantially more effective than the cold shoe in the 2" cartridge, thus steeper thermal gradients and possibly higher growth rates will be obtained. Second, the helium used to conduct heat from the interface to the heat sinks is introduced near the growth interface. As a result, the meniscus will be constantly flushed by the clean gas and less helium will be introduced into the cartridge, thus improving the effectiveness of the insulating elements. This change may therefore yield both cleaner ribbons and higher

growth rates.

Any growth run produces from 1 - 10 ribbons. Process variables (growth rate, meniscus height, gas composition, etc.) might also be tested during any of the experiments above (the possible disadvantage to concurrently investigating these other variables during an experiment might be that the effect of length of material grown on material character might be obscured). All of the above growth runs assume a 10 Ω cm melt because the nature of certain impurities is more easily characterized in higher resistivity material.

B. Machine Design

The parts for the 3" cartridge (Figs. 2 and 3) are arriving. Initial 3" growth runs are planned for the second week of May. Three 3" top heat shield packages were fabricated and have been delivered. Design of a 3" continuous puller is nearly completed and many mechanical parts have already been delivered.

The 'cartridge' assembly is, essentially, a complete EFG ribbon growth system minus only the crucible and main heating element. (See Section III.) It is comprised of a die, a series of horizontal and vertical thermal gradient control elements, a ribbon guide, and control thermocouples, all packaged to assure precise element alignment. Complete cartridge assemblies can be interchanged during a run.

The 2" cartridge currently in use in growth systems JPL No. 1 and JPL No. 3A has performed very well. Moderately low stress ribbon can be grown reproducibly 2" wide at $\sim 2"/\text{min}$. Rates over 2"/min have been obtained.

The goal of the current program is to reproducibly grow, at 3"/min, 3" wide ribbon suitable for solar cell preparation. Because of the success of the 2" cartridge assembly, it was used as the design base for the 3" assembly. Elements such as die, die heaters, heat shields, and linear cooling block were simply lengthened to fit the 3" dimension. Longer heater elements required beefing up the attendant power supplies, longer heat shields required new supports. The cartridge walls are now all graphite instead of stainless steel and graphite, water connections in the cartridge top are simplified. The greatest design changes are in the three lowest elements in the thermal gradient control system. Unlike the previous design, where die face heaters and end heaters were on different horizons, the 3" system die heaters are all on one plane. Their relative effectiveness will be equalized and more easily controlled. The number of heat shields between the die

Fig. 2. 3" cartridge, section view.

Fig. 3. 3" cartridge - detail.

top and the heat sinks is increased from 2 to 5, 6, or 7 (parts for each are ordered and an optimum number will be determined empirically). This increase will effectively increase the thermal gradient around the die top. The heat sinks have been extensively modified. The operating face temperature of the current design heat sinks is presumed to be $\sim 800^{\circ} - 1000^{\circ}\text{C}$, $300^{\circ} - 400^{\circ}$ higher than desired. To increase the effective cooling of the faces, the water flow capacity was increased, the water now flows in direct contact with the molybdenum block, and the heat sinks are machined from one piece of metal instead of three (a grafoil cushion between the molybdenum and stainless steel elements is eliminated). The entire heat sink including water tubes is now molybdenum. Finally, to grow at high rates, a helium-argon mixture has been needed to increase heat conduction from the ribbon to the molybdenum faces. In the 2" cartridge the gas is introduced through the linear cooling block wall, far from the interface. This not only reduced its direct effectiveness, but also provided a helium flow to the entire cartridge reducing the effectiveness of all its insulation. In the 3" cartridge, the gas mixture flows out of the heat sink faces. The volume of gas required will thereby be reduced and the gas flow will, in addition, continuously flush the liquid meniscus. If the effectiveness of the heat sinks is sufficiently increased by the design changes, the use of helium may not be necessary, even for 3"/min growth.

C. Stress Analysis

There are two interrelated problems with regard to thermal stresses in the growth of ribbon crystals of silicon: one is to minimize the extent of plastic deformation and, therefore, the strain induced imperfections, the other is to reduce, to a tolerable level, the residual elastic stress in the crystal when it reaches room temperature. The details of the theoretical and experimental approaches to the stress problem were described in previous reports. ^(1,2)

The major effort to date has been to reduce the residual stress in the ribbon while, at the same time, maintaining the desired fast growth rates. An experimental scheme to achieve this (via the cooling block/afterheater configuration in the cartridge) has come about, based on the theoretical understanding of the effects of the vertical temperature profile on the thermal stresses in the ribbon during growth, and on the empirical recognition of stress relaxation effects in silicon as a function of temperature. Growth rates of 5 cm/min for ribbon widths of 5 cm were achieved

in this program; the ribbons were essentially free of residual stress.

The basic limitations to a useful theoretical solution to either the problem of residual stress or that of the defect density lie in the insufficiency of plastic deformation data for silicon, and in the complexity and non-uniformity of the crystalline structure of the ribbons. As for the case of the residual stress, the defect density problem is, therefore, also being approached in a manner which is mostly experimental. Thus, correlations are sought between the defect densities and distributions, and the thermal profile in the growing ribbon. The latter is determined from experimental data on the thermal environment conditions (i.e., the cooling block/afterheater parameters) and growth rate using a computer program described previously.^(1, 2) Since the major experimental effort during this quarter has been directed towards the improvement of the chemical quality of the ribbons, there is no data to report at this time on such correlations between defect densities and thermal profiles. Some analytical results on typical dislocation densities and distributions in ribbons grown previously on this program are presented elsewhere in this report.

An extension to the theoretical stress analysis which has been considered is to attempt to predict the plastic strain induced defect density and distribution in the ribbon, and to compare the results with experimental observations of the defect density. A review of the relevant literature (e.g., Refs. 3 - 6) shows that the following procedure is generally used in such calculations: (i) the steady-state temperature distribution in a stationary crystal is first calculated; (ii) the thermoelastic stresses are determined (usually assuming that the solid is isotropic and that the modulus and coefficient of expansion are independent of temperature) - analytic solutions are possible only for simple stress and/or temperature distributions; (iii) the volume distribution of thermoelastic shearing stresses is compared with the corresponding plastic yield stress which is determined in independent experiments; (iv) the density of dislocations is calculated from an expression of the form

$$N = \frac{1}{b\ell} \cdot \frac{\tau - \tau_{CR}}{G},$$

where τ is the thermoelastic shear stress for a given slip system, τ_{CR} is the effective critical shear stress, G is the shear modulus, b is the Burgers' vector of the dislocations, and ℓ is the mean path traversed by the dislocations in the slip plane (it is assumed to be less than the cross-sectional dimension of the crystal).

It is implicitly assumed in this analysis that the amount of plastic flow is so small that the stress distribution remains unchanged, i.e., that the thermal strain is mostly elastic. Alternatively, one could consider the situation where the thermal strain is entirely plastic and all the stresses vanish (i.e., in essence, $\tau_{CR} = 0$). The applicability of the thermoelastic solution to this latter case is questionable, however. For either case, it is generally assumed that the dislocation density in the grown crystal is determined by the slip system for which the combination of τ , τ_{CR} and ℓ in the above expression results in a maximum dislocation density.

Another simplification which is used in the above analyses is that the motion of the crystal can be neglected in calculating the thermal stress induced defect density. In other words, no account is taken of the constantly changing stress distributions (and defect density) in a given transverse element of the crystal from the moment the element has solidified until it has reached room temperature. The dislocation distribution in this element, which must be the same as in any other element along the crystal growth axis, is assumed to come about as a result of the variables $\tau - \tau_{CR} - \ell$ attaining their "optimum" combination for maximum dislocation density, as explained earlier, at some point during cool-down. For each portion of this element, the maximum will occur, in general, at a different distance from the growth interface. Time dependent plastic flow effects and cumulative effects of the axial and radial gradients are thus excluded from the analysis.

Our analysis⁽¹⁾ of thermal stresses in silicon ribbons has been completely analogous thus far to the procedure outlined above. The calculations show, however, that the extent of plastic deformation is quite large (e.g., Table II in Ref. 1); the calculated thermal stresses, for a thermal profile which is appropriate for radiation into a 0°K environment, exceed the yield stress at all points in the growing ribbon from the melting temperature down to $\sim 600^{\circ}\text{C}$. Since, on the time scale of EFG silicon ribbon growth, plastic deformation can readily occur, and, in fact, stress relaxation above $\sim 1200^{\circ}\text{C}$ is found to be essentially complete,⁽¹⁾ the thermoelastic solution is thus no longer applicable. Clearly, one needs to incorporate inelastic stress-strain relations and time dependent effects into the solution.

To demonstrate the ineffectiveness of the linear elastic solution, we consider a ribbon which is initially stationary. In the region where the temperature exceeds $\sim 1200^{\circ}\text{C}$, the thermal stresses will be completely relieved by some appropriate amount of plastic deformation; below 1200°C , the stresses will be reduced to the

yield stress. If we now commence ribbon growth, the next element which solidifies will no longer experience the same thermal stress field as the previous element at that location; as this element cools to room temperature, it will be continually exposed to a stress field which is different from that in the original stationary ribbon.

An overview of the literature (e.g., Ref. 6) on thermal stresses in inelastic systems shows that the ribbon growth problem is exceedingly complex, even when idealized plasticity models are used. The inclusion of microstructural considerations (crystalline structure, slip systems, etc.), and the uncertainty of the relationship between plastic strain and dislocation density further complicate the problem. We will therefore not attempt any modeling of the inelastic thermal stresses in the ribbon on the current program. Our interest is clearly in obtaining experimental measures of the residual stress and of the defect density in the ribbons, and in correlating these with the ribbon growth conditions (thermal profiles, growth rate, ribbon dimensions). For our purposes, it is thus sufficient to establish a "figure of merit" for residual stress or defect density based on the temperature distributions in the ribbon which can be calculated from the growth conditions. This information is already contained in the thermoelastic solution. For example, the residual stress can be correlated to the non-linearity of the vertical profile in the ribbon from $\sim 1200^{\circ}\text{C}$ to $\sim 600^{\circ}\text{C}$. Similarly, we will use the thermoelastic solution (and the procedure described above) to obtain the maximum dislocation density in the ribbon, albeit we recognize that this solution is, at best, only qualitative. As indicated above, then, in the main the stress analysis work will be closely tied to the ribbon growth and defect characterization efforts.

III. GROWTH STATION NO. 3A (MACHINE 16) - MULTIPLE FURNACE

A. History of the Project and Description of Equipment

Since January 1975, a set of equipment intended to be a prototype production system for silicon ribbon has been under development at Mobil Tyco. At the time this design work was begun, silicon ribbon was being grown on a small laboratory scale in equipment adapted from other crystal growth processes. The goal of the design and development project undertaken at that time was to create a completely new system for EFG ribbon with greatly improved stability, efficiency, and productivity. Early (and subsequent) economic analyses of EFG-based solar cell manufacturing showed that a crucial cost element would be ribbon area produced per operator hour. An obvious means of increasing this ratio was to bring a number of ribbon crystals growing simultaneously under the surveillance of an operator in a single machine. This rationale led to the most outstanding characteristic of this system, its multiple ribbon growing stations.

The system consists of a furnace and associated equipment common to all growing stations, plus the individual growing stations composed of several subsystems.

The furnace, shown in Figure 4, has a cylindrical configuration with horizontal axis. A cylindrical hot zone containing the crucible filled with silicon, heating elements, and insulation, is housed within a water-jacketed steel chamber. A cross section through the furnace, Figure 5, shows the double walls of the outer chamber, the top opening through which the growth system is inserted, the two viewing openings, the hot zone with its insulating material, the three heating elements, and the crucible containing silicon. The heating elements and insulating materials are of graphite, as is the crucible holder which supports the quartz crucible.

The heating elements, of solid graphite, are approximately 90° segments cut from a long hollow cylinder. They surround the crucible on the bottom and two sides. The insulation is made in cylindrical form of two types of graphite-based material.

Fig. 4. Photograph of multiple ribbon furnace, Machine JPL No. 3A.

Fig. 5. Cross Section through Multiple Ribbon Furnace Machine JPL No. 3A.

Approximately half the thickness of the insulation is comprised of layers of Grafoil (Union Carbide) flexible sheet graphite, a material whose relatively low emissivity makes it effective as radiation shielding on the hot wall of such a furnace structure. Alternate flat and corrugated layers are cemented together into a cylinder with relatively low radial thermal conductivity. The low permeability of Grafoil makes it highly resistant to reaction with silicon monoxide, a desirable characteristic for use in this furnace.

Cemented to the outside of the Grafoil cylinder is a second cylinder of a fibrous graphite material known as Fiberform (Fiber Materials, Inc.). The whole composite cylinder is split in half along the horizontal centerline so that access may be gained to the crucible by lifting off the top half. The two halves of the insulation are installed in the stainless steel hot zone enclosure. This structure provides strength for the insulation, and mounting surfaces for the hardware supporting the crucible, heating elements, and other components. Openings are machined in the insulation for the growth systems inserted from above, for the heating element supports, and crucible supports.

The hot zone is attached to one of the round end plates of the furnace chamber, and all electrical and fluid connections to it are fed through this plate. The complete hot zone assembly is slid out of the furnace chamber onto a wheeled cart for all servicing. (Figure 6).

AC power from a three-phase 25kW phase-angle controlled power supply is fed to the heating elements at 15 volts. The elements are connected in "Y" configuration and are mounted on flexible supports which allow thermal expansion.

Temperature of the hot zone is monitored by two thermocouples located in the crucible supports, one of which is connected to a three-term temperature control instrument.

The atmosphere in the furnace during operation is argon at atmospheric pressure. The openings through which the growth system cartridges are inserted are not hermetic, so a continuous outflow of argon is maintained. Before starting the furnace, these openings are plugged, the chamber is evacuated by a mechanical pump, and then it is backfilled with argon. Argon enters the furnace through two flow meters, one feeding a manifold lying along the bottom of the chamber, the other connected to a pair of inlets feeding argon into the interior of the hot zone, one at each end.

Fig. 6. Photograph of furnace with the interior parts slid out onto service cart.

The subsystems comprising each of the multiple growth stations are growth system cartridge, continuous puller, cartridge power supply, and control systems. The growth system cartridge, Figure 7, is a unique outgrowth of this multiple ribbon furnace project. After its functioning was demonstrated in mid-1976, it was directly adopted by the single-station horizontal axis ribbon furnace (JPL No. 1) built under this contract.

The growth system cartridge is an assembly of all critical components associated with EFG ribbon growth. These components include die, die heaters, control thermocouples, radiation shields, heat removal elements, and afterheater. They are assembled in a graphite boxlike structure which holds them in precise alignment and isolates them from the furnace atmosphere and thermal environment. The three independently variable die heaters permit control of meniscus height and ribbon width. A steep vertical temperature gradient at the die tip, conducive to high speed growth, is produced by the flow of heat from the die heaters just below the die-top radiation shields, through the die and ribbon, to the water-cooled heat removal elements just above those shields. This steep gradient is only maintained for a few millimeters, through the heat removal elements, whereupon the ribbon enters the afterheater. The afterheater is a pair of thick parallel graphite plates whose lower ends are heated and whose top ends are connected to a heat sink. The structure is insulated on the sides so that the principal heat flow is vertical. The result of this heat flow is a nearly linear temperature gradient in the walls seen by the ribbon, which the temperature in the ribbon closely tracks as it cools. The hot end of the afterheater, or "linear cooling plates" as the structure is also called, is heated to a temperature at which silicon can relieve stresses formed during initial rapid cooling. Cooling from this point where stress relaxation is no longer possible takes place in a uniform axial gradient, resulting in low-stress ribbon.

The cartridge is assembled remotely from the furnace and is lowered into place after the silicon has melted. A power supply consisting of four transformers and four solid-state power controllers is associated with each cartridge. The transformers feed, respectively, the die face heater, die left and right end heaters, and the afterheater element. Six heater current leads, two pairs of thermocouple leads, two water connections, and one helium/argon line are attached to the cartridge before it is lowered.

Fig. 7. Cross Section through Growth Cartridge.

The ribbon puller has rubber/fabric belts between which the ribbon is gripped by pressure from an air pillow behind one of them. The puller is mounted to a pair of vertical rods on which it is raised and lowered by a small motor; the cartridge is coupled to the puller and the two are lowered as a unit. The opening through which the cartridge is inserted is fitted with an air lock and door system operated by a lever adjacent to the opening. When the cartridge is removed, one pair of doors closes upward to block air flow into the opening in the furnace chamber; another pair of doors simultaneously closes downward to block radiation from the opening in the hot zone.

Ribbon growth is visually controlled by an operator viewing the die top through a stereo microscope at an angle of 13 degrees up from the horizontal. Identical paths to the die top are provided from both sides of the furnace. In front of each ribbon station is a small control panel fitted with the following controls: die temperature set point, die heater power, pull speed, temperature ramp start/stop, temperature ramp magnitude, and cartridge raise/lower. These controls are the complete set required to initiate and manually maintain growth.

Ribbons issuing from the machine are presently manually scribed and broken at intervals of about 18 inches. A device to do this automatically is being designed.

The crucible in this furnace holds about 150 cm^3 of silicon per growth station. This is sufficient material for 12 m of ribbon of 5 cm x .025 cm cross sectional dimensions.

B. Experimental Activity in the Past Quarter

The furnace underwent its first major modification and cleanup in its $1\frac{1}{2}$ year existence during January, February, and March. The modifications were primarily intended to remove and reduce sources of contamination of the melt. Prior to this overhaul, the system was under general development and certain materials and procedures not compatible with the production of ribbon of good electronic quality were used. Material from this furnace has not been made into solar cells. With the resumption of growth activity in mid-March, the system is being operated with the intention of producing solar-cell quality ribbon. Major aspects of the new "clean" mode of operation are as follows:

1. The lab in which the furnace is located has been thoroughly cleaned; metal working tools and other sources of particulate contamination have been re-

moved; the immediate area of the furnace has been enclosed by curtains; within this area ceiling tiles have been replaced by non-particulating material.

2. A new insulation package which has been halogen purified has been installed. All other graphite parts used in the furnace and growth system cartridges have been halogen purified as well.
3. The furnace chamber was coated inside and out with FEP to stop rusting of weld area and to reduce the amount of water adsorbed by the inner wall between runs.
4. The previously described trap doors for cartridge openings were installed, greatly reducing the quantity of air admitted to the furnace, and eliminating a previous "dirty" method of blocking radiation from cartridge openings.
5. All assembly work is done by persons wearing vinyl gloves. Those operations which can be done in the laminar flow bench (assembling cartridges, loading crucibles, etc.) are done there.

C. Automatic Controls

1. Introduction

The long range goal of an automatic controls effort for crystal growth is to develop a control system to maintain tight geometrical tolerances on the cross-section of the growing crystal for an indefinite length of time with no involvement of a human supervisor. The achievement of such a goal would necessarily require the development of a detailed knowledge of the dynamic crystal growth process; additionally, an assessment of all possible types of random events, i.e., perturbations occurring during the process, must be made. Although dynamic models of the growth process have been formulated, much of this information is currently only qualitatively understood.

This knowledge has, nonetheless, been adequate for us to have been able to take the first step towards developing a long term control system. A sensitive technique for the determination of the process status has been developed. For a typical thermal geometry, use of this technique with associated control systems apparently has not required a direct temperature distribution determination in the growth system. The experimental version of this control system has previously been tested

on growth system 3A briefly (about 6 hours) before the initiation of this contract. Thus, only qualitative assessments of system performance have been made. Findings were that growth was indeed more stable using the system than with the system omitted; and some half hour "hands-off" periods of control were obtained. However, what constitutes good control performance? This is a difficult question to answer but we address it below.

Previous efforts at MTSEC have produced a basic control system. Under the contract, consistent with the level of effort to be expended, we intend to determine the control inadequacies of this system and to develop a deeper understanding of the relationships between the growth variables. With the time and effort allotted here, the overall milestone of this task will be to develop adequate technology to allow one operator to supervise ribbon growth from the five stations of 3A while maintaining the specifications on the crystal geometry.

2. Task No. 12 Statement of Subtasks

a. Installation of Three AWC Basic Systems: The project was begun with the installation of three basic AWC systems already built by MTSEC, on the JPL No. 3A crystal growth station on which all automatic control experiments will be carried out.

b. Techniques for Evaluation of System Performance: Crystal Geometry: Quantitative standards for crystal shape need to be established. First, specifications for performance will be generated; the hardware to record the appropriate data will be assembled. Initially, data will be collected on chart recorders, but later during this subtask other techniques may be used especially if it is found that several variables need to be recorded.

c. Techniques for Evaluation of System Performance: Thermal Geometry: A correlation of the crystal geometry to the temperature distribution across the die top should enhance the eventual development of more reliable control systems. Work on this task will generally be complicated by the need to make reliable temperature measurements on the die while not interfering with the growth process. Thus, the goal of this task will be to make these measurements simultaneously with the other process variables during growth.

d. Testing and Performance of Single AWC: Growth from a single cartridge will be controlled by a single AWC. The apparatus called for in (b) and

(c) will be installed and the system will be optimally tuned to approach the desired crystal geometry specifications called for in (b). Also, correlations to the temperature distributions will be made.

e. Testing and Performance of Adjacent Control Systems: A second cartridge will be put in place adjacent to the station controlled by the AWC. We will determine the extent to which the performance of the AWC controlled station is affected by the presence, then the operation, of the second cartridge. Finally, the two systems will be controlled by the AWC systems.

f. Testing and Performance of Control System with Two Adjacent Growth Systems: The same procedure as in (e) will be carried out except that a third cartridge will be added.

g. Maintenance of Performance During Adjacent Cartridge Removal: During multiple growth it may be occasionally necessary to remove a cartridge from the system. This task is undertaken to resolve how this will affect the performance of AWC controlled cartridges adjacent to the removed cartridge.

h. Monitoring Improvements to AWC: In order to reduce the fatigue to the supervisor of AWC growth, certain improvements to the system are anticipated. These include alarms to notify the operator that the growth system is beginning to go out of bounds (specification) or that a "freeze" has occurred. These alarms will be developed under this subtask.

i. Develop Improved Control System: If the basic AWC system initially employed fails to meet the specifications in (b), work will be initiated on a more sophisticated control system.

j. Build and Install Last Two AWC Systems: A total of five AWC controlled stations are called for. The last two added to the multiple furnace will incorporate the improvements of (h) as well as the potential improvements of Task (i).

k. Test Last Two Improved Control Systems: If Task (j) is implemented, then a period for testing the performance of the advanced systems is necessary. Also, during this task, the first three AWC systems would be updated.

1. Test Overall System Performance: All five automatically controlled cartridges will be tested simultaneously and supervised by one operator. This will also be attempted in the presence of melt replenishment.

3. Progress Since February 14, 1977

Subtask (a). Since the initiation of work under Modification No. 11 to the current contract, the electronic control units for three "Automatic Width Control" (AWC) systems have been installed in the growth station (Model 3A). Some of the electronics have been tested. However, the "head" units have required a minor modification and have not yet been installed and tested. The optics has been tested and is satisfactory.

Subtask (c). It has been concluded that we should consider cavities machined into the die top for optical temperature readings. This procedure would reduce the sensing of reflected radiation. Also, the emissivity of the surface near the die top is probably sensitive to the extent of all silicon infiltration and "slop over" during seeding. Currently, the observation of possible cavity locations is blocked by the die top radiation shields in the cartridge. Thus, notches may have to be made in these shields (which would further distort the local thermal geometry).

Due to the geometry of the die top, cavities would have to have a diameter of .030 inches or less. Also, the allowable aperture of the radiometer is limited by the narrow optical viewing channel from the die top to the viewport. The requirements seem to be inconsistent with commercially available units and a modification may be necessary.

IV. CHARACTERIZATION

As indicated before, the characterization effort divides into two different areas. Firstly, characterization of the material itself for instance with respect to its crystallographic and electrical properties, and secondly, characterization of the material as a solar cell.

The ultimate aim of course is to correlate solar cell performance with particular features of the crystallographic and chemical properties found in the material.

A. Materials Studies

1. Effect of Growth Rate on Defect Density

One of the criteria to be considered while growing ribbon at high growth rates is the possible effect of such rates on the "equilibrium defect structure" ⁽⁷⁾ and also the attendant effects of the thermal stress generated during growth on the defect density and defect distribution in the ribbon. The problem of "grown in" stress is of course being dealt with in detail in this contract (see Section II.C.) but some interesting data have already been gathered.

Sections of a ribbon were grown at different speeds ranging from 1.25 to 1.75 inches/min, with and without forced cooling in the resistance heating system. (JPL No. 3A). Forced cooling was used to increase the growth speed, while a powered after-heater was used to reduce the residual stress. The ribbon samples were examined for residual stress. (Table I) Defect densities were measured at 4 points across the width at 2 points in each section after preferentially etching the samples. The averages of the 8 measurements have been listed in Table I. As a reference, ribbons which are not stressed (grown at approximately 1 inch/min from induction heated systems) were also examined and the defect densities are listed in Table II. Two sections per ribbon were also examined in this instance, and these are listed as (A) and (B). It is obvious that increases in growth speed did not result in an increase

Table I. Defect Densities in Ribbons Grown
in JPL Machine No. 1.

Ribbon No.	Growth Speed (in./min)	Stressed (?)	Dislocation Density (No./cm ²)	Parallel Twin Density (No./cm)	Intersecting Boundary Density (No./cm ²)
16-042 (A)	1.25	No	4×10^5	9.2×10^2	-
16-042 (B)	1.25	No	1.2×10^6	1×10^3	-
16-042 (C)	1.75	Yes	6.9×10^5	1.1×10^3	4×10^2
16-042 (D)	1.5	Yes	5.1×10^5	7.3×10^2	2.5×10^2
16-042 (E)	1.5	No	3.1×10^5	1.8×10^2	-
16-042 (F)	1.5	No	1.3×10^6	4×10^2	9×10^2

Table II. Defect Densities in Ribbons Grown
in Induction Heated Systems.

Ribbon No.	Growth Speed (in./min)	Stressed (?)	Dislocation Density (No./cm ²)	Parallel Twin Density (No./cm)	Intersecting Boundary Density (No./cm ²)
12-582-1 (A)	1.0	No	3.6×10^5	2.9×10^2	-
12-582-1 (B)	1.0	No	1.9×10^5	25.6	-
12-583-1 (A)	1.0	No	$>10^6$	7.7×10^2	-
12-583-1 (B)	1.0	No	5.9×10^5	7.9×10^2	-
12-584-1 (A)	1.0	No	6.1×10^5	1.9×10^2	-
12-584-1 (B)	1.0	No	3.3×10^5	2.6×10^2	-
13-787-1 (A)	1.0	No	3×10^5	1.3×10^3	-
13-787-1 (B)	1.0	No	2×10^5	3.6×10^2	-
13-770-1 (A)	1.0	No	3.9×10^5	2×10^2	8.15×10^2
13-770-1 (B)	1.0	No	1.2×10^5	1.6×10^2	5.1×10^2
12-582-1 (A)	1.0	No	2.4×10^4	1.2×10^2	2.04×10^2
12-582-1 (B)	1.0	No	3×10^5	27.3	-
13-787-1 (A)	1.0	No	3×10^5	1.3×10^3	-
13-787-1 (B)	1.0	No	2×10^5	3.6×10^2	-
12-585-1 (A)	1.0	No	1.5×10^5	4.8×10^2	-
12-585-1 (B)	1.0	No	6.5×10^4	2.5×10^2	6×10^3

in the defect density. Thus, defect related properties of the as-grown material should remain unchanged in ribbons grown up to speeds of at least 1.75 inches/min.

2. Defect-Impurity Interactions

In order to fully examine the effect of crystallographic defects on base material properties, samples were chosen which were next to the seed. Seeds were (111) Czochralski slices. Diffusion lengths were measured, using the surface photovoltage (SPV) technique on as-grown samples which employed aluminum Schottky-barriers for current collection. The samples were subsequently preferentially etched to reveal the defect structure. The data are presented in Figure 8 a-c with the defect density shown being representative of the area under the Schottky barrier. As can be seen, measurable diffusion lengths were obtained only in the Czochralski seed region, with the diffusion length degrading to $24\ \mu\text{m}$ in the seed when it is next to the ribbon. In a region farthest from the seed-ribbon junction, the Czochralski seed had a diffusion length of $67\ \mu\text{m}$. Thus, at first sight one might conclude that the defects which were introduced into the Czochralski material adjacent to the initial ribbon growth did indeed decrease L_D from $67\ \mu\text{m}$. However, this conclusion would not necessarily be correct until it can be established that no impurities were transferred from the ribbon material into the adjacent Czochralski Si during the initial growth either by diffusion or through the gas phase.

In any event, in the adjacent ribbon material, L_D was found to be less than $2\ \mu\text{m}$, with the structure degraded only little more than in the Czochralski material. Hence we conclude that the crystallographic defects found are in any event not responsible for the decrease of L_D from $24\ \mu\text{m}$ to $< 2\ \mu\text{m}$.

In general we have concluded then from these and other experiments⁽⁸⁾ that chemical impurities play a significant role in the degradation of L_D in EFG ribbon material.

This view is further indirectly supported by comparison with the diffusion lengths of typical EFG material grown from induction heated systems (Figure 9 a-c) which are generally found to be in the range between 25 and $45\ \mu\text{m}$ by dark SPV measurements.

So far as we can determine. from analyzing many ribbon surfaces, there is no overall difference in the defect structure of induction furnace produced and resistance furnace produced ribbon; but there is a great difference in the construction materials found in the hot areas of these two types of furnaces. Hence we hold the view,

(a)
 $L_D = 67 \mu\text{m}$

(b)
 $L_D = 24 \mu\text{m}$

(c)
 $L_D = 0 \mu\text{m}$

Fig. 8. Preferentially etched regions of: a) Czochralski seed farthest from seed ribbon junction; b) Czochralski seed adjacent to initial ribbon growth; c) ribbon material near seed.

(a)
 $L_D = 0 \mu\text{m}$

(b)
 $L_D = 0 \mu\text{m}$

(c)
 $L_D = 38 \mu\text{m}$

Fig. 9. Preferentially etched regions of "typical" EFG material (3 different pieces).

that at present unintentionally introduced chemical impurities constitute the limiting factor to the advancement of solar cell efficiency in resistance furnace produced EFG material.

B. Investigations on Solar Cells

1. EBIC Studies

Preliminary data was presented in the last quarterly report on the effect of illumination on bulk diffusion length and on the effectiveness of recombination centers in solar cells fabricated on EFG silicon ribbons. The assumption was made that during illumination certain trap levels corresponding to impurities in the material are saturated, thus decreasing the detrimental effects due to these impurities. (2,8) In order to further understand the nature of the traps, EBIC measurements were made on a mesa diode fabricated from a finished solar cell. The effect of light intensity on the degree of recombination was examined in the mesa diode. An ELH lamp was used as the light source with incident intensity of 100 mW/cm^2 and the intensity was decreased using neutral density filters. The light source was placed external to the specimen chamber in the SEM, and was focussed on the diode through a quartz window placed on the side port of the instrument. Relative local recombination at crystallographic defects was measured from EBIC line-scan signal levels.

Figure 10 a-c shows the EBIC photograph and a corresponding line scan signal in (a) the dark (b) at 5.8% of incident intensity, and (c) at 100% intensity (i.e., 100 mW/cm^2). The electron beam forward biases the junction and the I-V characteristics of the device with and without the electron beam are shown in Figure 10 (d). Figure 11 shows the effect of "white" light on the degree of recombination at electrically active boundaries. Since the sampling depth at 30 keV electron accelerating voltage is approximately $6 \mu\text{m}$, an area enclosing the junction and regions of the base material close to the junction is essentially observed in the SEM.

From these experiments then we draw the conclusion, that the "light enhancement effect" on which we have previously reported is also effective with respect to local recombination. However, we cannot yet say whether this effect is centered solely in these microscopic regions of high recombination. We plan to publish more detailed findings on this "light enhancement effect" as determined by both optical and electron microscopic methods in the very near future. These publications should then complement the somewhat preliminary studies presented here and in Ref. 8.

Fig. 10. EBIC micrograph and corresponding line scan signal: a) in the dark; b) at 5.8% of AM1; c) at AM1 (100 mW/cm² ELH lamp); d) I-V characteristics of the device examined above (i) with and (ii) without the presence of the electron beam. (Scale: I = 10 μA/div., V = 0.1 V/div.)

Fig. 11. Effect of light intensity on the degree of recombination at electrically active boundaries.

2. Studies of I-V and Spectral Characteristics

In order to begin to obtain a more definite view on the suspected deficiencies of material from JPL No. 1, which have been reported previously, we chose two solar cells prepared from that material for more detailed examination.

Overall cell data for these two cells are:

Cell No.	Area (cm ²)	Reverse Leakage (mA)	V _{oc} (Volts)	I _{sc} (mA/cm ²)	F.F.	P _{max} mW/cm ²
8809	2.31	0.02	0.468	13.8	0.710	4.58
8813	2.31	0.016	0.486	15.54	0.739	3.54

These cells are not antireflection coated and though only very few cells have been processed, these are definitely the better ones so far seen from material produced in JPL No. 1. They were produced using standard POCl₃ diffusion. From the results above one may perhaps deduce that the low voltages and currents indicate material with fairly short lifetime, whereas the relatively good fill factors appear to reflect that the devices are not deficient in other respects. Spectral response was the first measurement made and the results are presented in Figure 12.

If one now uses an appropriate model relating the collection efficiency (Q) of the solar cell to the base diffusion length, one can extract the bulk diffusion length from the spectral response measurements. Such a model has been developed at Mobil Tyco by R. O. Bell. (See Appendix.) Aside from diffusion lengths (L_D) the model also yields the junction depths using appropriate curve fitting techniques. Thus, in Figure 12, the fitted curve is indicated by the line and the diffusion data and junction depths calculated are shown in the figure. These diffusion lengths and junction depths obtained at very low light levels can now be used to calculate the expected performance of a solar cell according to models of which we have discussed the principal features previously.⁽⁹⁾

When that is done, we calculate (using appropriate numbers for the fact that the cells mentioned above are not AR coated and covered by an ~ 8% coverage grid) the following values:

Fig. 12. Spectral Response of Cells No. 8809 and 8813

L_n (μm)	x_j (μm)	I_{sc} (mA/cm^2)	V_{oc}
8.44	0.33	11.3	0.476
10.7	0.21	13.2	0.499

Hence, we find that our cells show higher currents than those appropriate for the diffusion lengths measured, but lower voltages than those expected.

These differences cannot at the moment be reconciled, but again, it is apparent that they may be related to the details of light induced detrapping or trap filling which we assume is the origin for the light enhancement effect. But until a definite model for such an effect has been worked out, it appears impossible to even try and reconcile the differences presented above.

3. Infrared Scans

The two cells mentioned above were further investigated using infrared scanning techniques which also have been described previously.⁽⁸⁾ The 1 cm width of the cell was examined in the scans, the wavelength of the beam being $0.95 \mu\text{m}$. The IR scans were repeated with the sample illuminated from an ELH lamp (corresponding to $100 \text{ mW}/\text{cm}^2$ incident radiation). Spectral response data were gathered on the same cells and an effective diffusion length, both in 'dark' and under illumination, was calculated from the spectral response data using the solar cell model and procedure described in the Appendix. The diffusion lengths thus obtained were used to calibrate the signal levels observed in the IR scans. The IR scan data are shown in Figures 13 (a) and 14 (a). In order to correlate the bulk diffusion length to the electrical activity of defects near the junction, EBIC scans were made on the cells and are shown in Figures 13 (b) and 14 (b). Even though correlations could be obtained between the IR and EBIC scans, a point-by-point correlation was not possible because of the lower resolution (due to the larger spot size employed) of the IR scans. The junction was subsequently removed in these cells by mechanical polishing and photomicrographs obtained after preferential etching (Figures 13 (c) and 14 (c)). The arrow points to general areas in the IR, EBIC, and photomicrographs where correlations exist. Once again, the fact that only a very small percentage of the total number of crystallographic features are electrically active is in accordance with the hypothesis that crystallographic defects alone are not the significant detriment to solar cell performance at the present time, but that defect-impurity inter-

(a)

(b)

(c)

Fig. 13. Cell No. 8809: a) IR scan; b) EBIC image; c) micrograph of etched specimens showing boundaries.

(a)

(b)

(c)

Fig. 14. Cell No. 8813: a) IR scan; b) EBIC image; c) micrograph of etched specimens showing boundaries.

actions constitute the main impediment. Since the EFG growth process leads to a largely fixed defect structure⁽⁷⁾ the only option to improve the performance of EFG cells then lies in improving the chemical purity of the ribbon.

However, the "light enhancement effect" which we have so prominently mentioned throughout this discussion causes significant increases of the operational L_D under AMI conditions when compared with "dark" L_D measurements. Thus actual solar cell performance is better than that which is deduced from dark L_D measurements. However, until the cause for the "light enhancement" is definitely established it appears fruitless to try and quantify the differences between solar cell performance in materials from different machines.

What can be unequivocally said nevertheless is, that the better quality material always has the larger dark drift length. How that translates into solar cell performance, however, considering both the "light enhancement effect" and the general inhomogeneity found in the cells as evidenced in both IR scans and EBIC investigations is much less clear.

4. Standardization of Solar Cell Processing

To deduce materials properties from solar cell performance, spectral response measurements, analysis of the total I-V curve, and scanning techniques are the three major methods we apply.

They are all using some kind of mathematical modelling technique on the experimental results obtained, in order to extract more basic data, and our particular model is presented in Appendix 7.

However, if one wants to be quantitatively successful with such techniques a fair amount of standardization of the solar cell process is a necessity so that variables which are not directly related to materials performance are unchanged from cell to cell and also conform reasonably well to the current "general state of the art" to allow comparison with other results.

We have therefore taken steps to develop such a "standard" process with some slight differences when it was applied to ribbon in order to demonstrate some ways in which ribbon cell performance can be optimized. The process and the attendant results are described below.

a. The "Standard Process"

The Standard Process used is shown in Table III. Particular care was taken to design a metal mask with minimum grid shadowing of the cell by keeping the finger and, particularly, the busbar widths to a minimum. Metal series resistance is kept low by solder dipping the cell to build up the contact thickness. Figure 15 shows a nominal 1 inch by 4 inch ribbon cell having this pattern. Two contact pads approximately 1/4 and 3/4 along the busbar are provided for connection. The metal coverage of this pattern is approximately 7.9%.

TABLE III . SUMMARY OF CELL FABRICATION PROCESS

No.	Step	Description
1	Pre-Diffusion Clean	Hot H_2SO_4 clean, HF oxide etch, hot HNO_3 clean, rinse, and dry
2	N^+ Diffusion	Phosphorous (PH_3) diffusion, 900°C , 30 min.
3	Back Surface P^+ Diffusion	Etch remove back-side N^+ layer, vacuum evaporate Al, 825°C diffusion
4	Front Oxide Etch	Buffered HF
5	Metallization	Cr-Ti-Ag through a metal mask
6	Sinter	450°C , 10 min, forming gas
7	Junction Edge Clean-up	Scribe, break and etch all cell edges
8	Solder Dip	62 Sn - 36 Pb - 2 Ag
9	AR Coat	Vacuum evaporate $\sim 700 \text{ \AA}$ SiO

Another area where optimization was performed was in antireflection coating.

To test both the process and optimize the AR coating thickness, several 1" x 2" Czochralski cells were fabricated.

Summarized in Table IV are the results on these cells as tested with a simulator employing ELH lamps at 100 mW/cm^2 . Results both before solder dipping and AR coating, and after solder dipping and various thicknesses of SiO AR coating are shown. As can be seen, these rather large area Czochralski cells made by the "standard" process possess efficiencies up to 14%, depending on the AR coating optimization. The process therefore clearly makes good use of the basic ma-

Fig. 15. Photograph of a 1" x 4" (nominal) EFG ribbon solar cell showing low area coverage grid pattern.

terials properties.

It should of course be noted here, that this process, although adopted as "standard" here is not standard in comparison with most other known solar cell processes. Indeed, the PH_3 diffusion was specifically developed at Mobil Tyco's own expense before this contract started because it produces highly reproducible results when applied to EFG ribbons.

Table IV. AMI test results of Czochralski solar cells made using the "standard" process. The upper results are before soldering and AR coating; the lower ones are after.

Cell No.	V _{oc} (mV)	J _{sc} (mA/cm ²)	P _{max} /A (mW/cm ²)	Fill Factor	Area (cm ²)	Remarks
J-40	582	21.61	9.92	0.789	9.07	
41	577	20.43	9.33	0.791	9.01	
42	579	21.41	9.84	0.794	8.74	
43	579	21.18	9.55	0.779	9.11	
44	577	19.92	9.20	0.801	9.24	
45	579	21.35	9.42	0.762	9.13	
40	594	30.65	14.33	0.787	9.07	700 Å SiO ₂
42	590	29.98	13.84	0.782	8.74	650 Å
43	590	30.4	13.5	0.753	9.11	725 Å
44	592	28.9	13.2	0.772	9.24	675 Å
45	594	30.5	14.0	0.772	9.13	750 Å

Although the results are not statistically meaningful, it appears that a true blue color (thickness $> 700 \text{ \AA}$ of SiO) gives a slightly higher I_{sc} increase than a violet colored film ($< 700 \text{ \AA}$).

Tables V and VI present results on EFG cells where a second optimization step has been introduced, namely texture etching (which indeed does work on EFG material !)

It appears that H_2SO_4 based etches do give improved performance although the details as to why seem still somewhat elusive. On average though, this etching step gives very good, uniform performance of 9 - 10% in 6 cells of varying areas up to 1" - 4". Again then, the process makes good use of the basic materials properties.

Very recently, yet different pre-etching steps using a simple silicon etch were employed and also R.F. furnace grown material of somewhat higher diffusion length was used. But otherwise the exact steps described in Table III were executed. The results are shown in Table VII. These are clearly the highest efficiencies we have ever observed in EFG cells, particularly for the 1" - 4" size. They not only demonstrate the basic capability of the material to achieve high efficiency but they also again show the validity of the "standard" process.

It should be noted that in all these cases, the improvement in I_{sc} due to the SiO coating was $\sim 42\%$. The coating was evaporated onto a cold Si surface and not baked, thus degradation of these coatings with time may be expected in accordance with previous experience in solar cell manufacturing. Nevertheless, the results shown do certainly establish that fairly high solar cell efficiencies should be achievable with EFG material if a process properly tailored to it is used.

Table V. AMI test results of cells made from Ribbon 13-793-1 before soldering and AR coating.

Cell No.	V _{oc} (mV)	J _{sc} (mA/cm ²)	P _{max} /A (mW/cm ²)	Fill Factor	Area (cm ²)	Remarks
26	528	19.08	6.66	0.661	20.13	$\left. \begin{array}{l} \text{H}_2\text{SO}_4\text{-4:0:1} \\ \text{Textured surface etch} \end{array} \right\}$
27A	528	19.21	6.29	0.620	11.29	
29	534	19.71	7.18	0.683	5.43	
30	534	19.97	7.56	0.699	5.16	
31	542	19.54	7.36	0.695	3.53	
23B	532	19.1	6.88	0.676	9.3	
38	514	17.67	5.83	0.642	16.98	$\left. \begin{array}{l} \text{KOH} \\ \text{Textured surface etch} \end{array} \right\}$
46	513	19.23	5.96	0.604	10.40	
47	503	17.72	5.30	0.595	6.04	
48	499	18.47	4.93	0.534	4.87	
49	525	18.36	5.05	0.524	8.71	
21A	531	19.0	6.60	0.653	10.6	$\left\{ \begin{array}{l} \text{No textured surface} \\ \text{or pre-diffusion etch} \end{array} \right.$

Table VI. AM1 test results of cells from Ribbon 13-793-1
after soldering and AR coating.

Cell No.	V _{oc} (mV)	J _{sc} (mA/cm ²)	P _{max} /A (mW/cm ²)	Fill Factor	Area (cm ²)	Remarks
23B	540	25.26	9.03	0.662	4.87	$\begin{matrix} \circ \\ \text{A} \end{matrix} \text{SiO} \left. \begin{matrix} 700 \\ 650 \\ 725 \\ 675 \\ 700 \\ 750 \end{matrix} \right\} \text{H}_2\text{SO}_4\text{-4:0:1} \\ \text{26} \quad 536 \quad 25.33 \quad 9.19 \quad 0.677 \quad 20.13 \quad \begin{matrix} \circ \\ \text{A} \end{matrix}$ $\left. \begin{matrix} \circ \\ \text{A} \end{matrix} \right\} \text{textured surface etch}$
27A	543	25.95	9.86	0.628	11.29	
29	544	26.15	9.76	0.686	5.43	
30	556	26.36	10.27	0.701	5.16	
31	554	26.06	10.05	0.700	3.53	
38	532	26.12	8.94	0.643	9.80	$\begin{matrix} \circ \\ \text{A} \end{matrix} \text{SiO} \left. \begin{matrix} 750 \\ 700 \\ 650 \\ 725 \\ 675 \end{matrix} \right\} \text{KOH textured surface etch}$
46	530	26.05	8.89	0.644	10.40	
47	520	23.6	7.45	0.607	6.04	
48	521	25.05	6.85	0.525	4.87	
49	542	24.82	8.47	0.630	8.74	
21A	546	25.40	9.14	0.660	10.6	$\begin{matrix} \circ \\ \text{A} \end{matrix} \text{SiO} \left. \begin{matrix} 700 \end{matrix} \right\} \text{No textured surface or pre-diffusion etch}$

Table VII. AM1 test results of EFG ribbon cells which received a pre-diffusion Si etch (9:1 HNO₃-HF, 1 min) (Ribbon No. 12-591, RF grown).

Cell No.	V _{oc} (mV)	J _{sc} (mA/cm ²)	P _{max} /A (mW/cm ²)	Fill Factor	I _{REV} (mA)	Area (cm ²)
J-55	559	28.61	11.52	0.720	2.96	19.83
57A	546	27.43	10.90	0.728	0.15	7.56
57B	561	28.39	12.02	0.755	0.75	6.03

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APPENDICES

1. Updated Program Plans

On March 3 and 4, 1977 Dr. M. Leipold visited at Mobil Tyco to discuss progress in the contract to date and plans for the tasks just started under Uni-lateral Modification No. 11. Since detailed program plans are not called for in Uni-lateral Modification No. 11, only informal plans, but including milestone charts and task descriptions, have been sent to Dr. Leipold. We are now working on all tasks according to these informal plans.

2. Man Hours and Cost

Previous man hours were 8,048 and cost plus fixed fee was \$265,603. Man hours for January plus February were 1863 and cost plus fee was \$52,491. Man hours and cost for March are estimated to be 1,841 and \$65,442 respectively. Therefore the first quarter of 1977 man hours are estimated to be 3704 and cost plus fee to be \$117,933. Total cumulative man hours and cost plus fixed fee are estimated to be 11,752 and \$383,536 respectively.

3. Engineering Drawings and Sketches Generated During the Reporting Period

See Figures 1, 2, 3, 5, and 7 in the body of the report.

4. Summary of Characterization Data Generated During the Reporting Period

These data are presented in Section IV of this report. They are very hard to summarize without being misleading. Thus, Section IV should be consulted directly.

5. Action Items Required by JPL

None

6. New Technology During This Reporting Period

None

7. Work not performed under the contract but introduced for technical clarification: Diffusion Length Measurements from Solar Cell Spectral Response by R. O. Bell
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One procedure we have used to determine the diffusion length in silicon is to examine the spectral response of a solar cell. Figure A1 shows this schematically. As a monochromator illuminates the solar cell, the short circuit current is measured. If we know the intensity, we can calculate the charge collection efficiency and from that and the model discussed below deduce some of the properties of the solar cell and the material from which it is fabricated.

I. Model of Charge Collection in a Solar Cell

In order to use physical measurements to extract material parameters from a device, it is necessary to have a model that connects the fundamental properties to the response. This can generally be done on a number of different levels of complexity. This section discusses the model developed at Mobil Tyco and used to extract diffusion lengths and junction depths from spectral response measurements.

The model of a solar cell is taken in a one-dimensional approximation as shown in Figure A2. An n-type surface layer, d thick, is on a p-type base, T thick, and separated by a space charge region ℓ thick. In the n- and p-regions we assume charge collection is by diffusion, but because of the built in electric field in the space charge region, essentially 100% charge collection occurs.

This model is substantially more complicated and realistic than usually used for data analysis but (in order to keep the programming and computer costs reasonable) not as sophisticated or involved as sometimes used in theoretical modeling of solar cells.

A. Charge Collection from p-Region

The basic equations governing charge collection in the p-region where electrons are the minority carriers are

Fig. 1. Experimental arrangement used to measure spectral response of solar cells.

Fig. 2. Geometry used to model n on p solar cell. The light is normally incident on the n-region. Total reflection is assumed to occur at the back surface.

$$\frac{\partial n}{\partial t} = U + G + \frac{1}{q} \frac{dJ_n}{dx} \quad (1a)$$

$$J_n = q\mu_n nE + qD_n \frac{dn}{dx} \quad (1b)$$

where U is the net internal recombination-generation rate, G is the generation rate due to external processes, q is the electronic charge, μ_n is the mobility of the electrons, and D_n is the diffusion coefficient of the electrons. For U and G take

$$U = \Delta n / \tau_n \quad (2)$$

$$G = \alpha [e^{-\alpha x} + e^{\alpha(x-2T)}] \quad (3)$$

where τ_n is the lifetime of the excess electron concentration, Δn , and α is the optical absorption coefficient. The second term on the right hand side of Eq. (3) arises from carriers generated by photons reflected from the back surface. We have assumed that a unit flux of photons is incident inside the solar cell and we will have to correct for the reflectivity later. We also assume we know α as function of wavelength, λ .

The boundary conditions we will use are that at the back surface and at the interface between the space charge and p-region the excess carrier concentration is zero.

We next assume the electric field is small enough to be neglected and consider equilibrium conditions where $\partial n / \partial t = 0$. The system of equations reduces to

$$\frac{d^2 \Delta n}{dx^2} - \frac{\Delta n}{L^2} + \frac{\alpha}{D_n} [e^{-\alpha x} + e^{\alpha(x-2T)}] \quad (4)$$

where we have set $L^2 = \sqrt{D_n \tau_n}$

The solution to this equation is

$$\Delta n = A e^{-\alpha x} + B e^{\alpha x} + C e^{x/L} + D e^{-x/L} \quad (5)$$

Substituting into Eq. (4) and equating the coefficients of $e^{\alpha x}$ and $e^{-\alpha x}$ determine A and B to be

$$A = \frac{\alpha L_n^2 / D_n}{1 - (\alpha L_n)^2} e^{-\alpha(d + \ell)} \quad (6)$$

$$B = A e^{-2\alpha T} \quad (7)$$

C and D are then determined from the boundary conditions.

We want to find the current at the interface from the base region J_B , i.e.,

$$J_B = q D_n \left. \frac{d\Delta n}{dx} \right|_{\text{inter}} = q D_n [\alpha(B - A) + \frac{1}{L} (C - D)] \quad (8)$$

After some manipulation we find

$$J_B = q \frac{\alpha L_n}{1 - \alpha^2 L^2} e^{-\alpha(d + \ell)} \left[\left\{ (1 - \alpha L) + \frac{e^{-T/L} - 2e^{-\alpha T}}{\sinh T/L} \right\} + \left\{ (1 + \alpha L) + \frac{e^{-T/L}}{\sinh T/L} \right\} e^{-2\alpha T} \right] \quad (9)$$

B. Charge Collection from Space Charge Region

Since all the charge generated in the space charge region, J_{sc} , is collected, this contribution is rather simply

$$J_{sc} = q [e^{-\alpha d} - e^{-\alpha(d + \ell)}] \quad (10)$$

C. Charge Collection from n-Region

The solution for the n-region proceeds similarly to that for the base except the contribution by reflection from the back has been neglected and slightly different boundary conditions are used, i.e.,

$$D_p \frac{d\Delta p}{dx} = S\Delta p \quad \text{at the front}$$

and $\Delta p = 0$ at the n-region, space charge interface.

The basic equation is that of Eq. (4) except the $e^{\alpha x}$ term is eliminated and all electron related parameters are replaced by hole parameters. The solution is

$$\Delta p = A e^{-\alpha x} + C x/L_p + D e^{-x/L_p} \quad (11)$$

Proceeding as above, we obtain for the contribution to the current, J_s ,

$$J_s = q \frac{\alpha L_p}{1 - \alpha^2 L_p^2} \left[\frac{\alpha L_p - e^{\alpha d} \sinh \frac{d}{L_p} + S \frac{\tau_p}{L_p} (1 - e^{-\alpha d} \cosh \frac{d}{L_p})}{S \frac{\tau_p}{L_p} \sinh d/L + \cosh d/L_p} - \alpha L_p e^{-\alpha d} \right] \quad (12)$$

The recombination at the surface is quite high (the order of 10^6 cm/sec) and the minority carrier diffusion length is small (the order of $0.1 \mu m$) so it is quite a good approximation to take

$$S \tau_p / L_p^2 \gg \alpha \quad \text{and} \quad S \tau_p / L_p \gg 1$$

Thus, J_s becomes

$$J_s = q \frac{\alpha L_p}{1 - \alpha^2 L_p^2} \left[(1 - \alpha L_p) e^{-\alpha d} + \frac{1 - e^{-\alpha d}}{\sinh d/L_p} \right] \quad (13)$$

The total charge collection efficiency, Q , is the sum of Eqs. (9), (10) and (13).

$$Q = (J_B + J_{sc} + J_s)/q \quad (14)$$

II. Data Analysis

A computer program has been written to fit the spectral response data to Eq. (14). The four variables that can be used as fitting parameters are a normalization

factor, N , L_n in the p-region, the junction depth d and L_p in the n-region. Generally only the first three parameters are fit and a value is assumed for L_p . A least square analysis program that works on non-linear equations is used. By least square we mean that if

$$D = \sum_{k=1}^K (Q_{\text{exp}} - Q_{\text{cal}})^2 \quad (15)$$

we adjust

$$\frac{\partial D}{\partial N} = 0, \quad \frac{\partial D}{\partial L_n} = 0, \quad \frac{\partial D}{\partial L_p} = 0 \text{ and } \frac{\partial D}{\partial d} = 0.$$

A computer program has been written to do this. The sum is over all the wavelengths measured. Q_{exp} is the measured value and Q_{cal} is Eq. (14) multiplied by the factor N .

Generally quite satisfactory fits are obtained if the calibration is good and the surface of the silicon is clean of anything that might affect the reflectivity. It is necessary that the experimental data be scaled to a constant photon flux at all wavelengths. An absolute calibration is not required since one of the parameters is a normalization factor. If a Schottky diode is being evaluated then d is generally set equal to zero.

Figure A3 shows the results for a ribbon cell. N , L_n and d were allowed to vary while ℓ , T_o and L_p were fixed at the values shown in the figure.

Fig. 3. Measured (points) and calculated (solid line) charge collection for EFG silicon solar cells L_n and d were variable parameters with l , T_0 and L_p fixed.