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LARGE AREA SILICON SHEET BY EFG

Fourth Quarterly Report for October 1—December 31, 1979

May 1, 1980

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

Mobil Tyco Solar Energy Corporation
Waltham, Massachusetts

U.S. Department of Energy

Solar Energy

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LARGE AREA SILICON SHEET BY EFG

Program Manager: F.V. Wald

Fourth Quarterly Report - Subcontract No. 954355

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"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

ABSTRACT

In Machine No. 1, studies concerning the influence of gas ambients on the properties of the ribbon grown from resistance heated machines have continued. It has been demonstrated that material grown in a CO₂-containing ambient can be processed so that cell efficiencies of ~12% (AM1) result.

Machine 3B, the multiple furnace, is still in preparation for its first 10 cm ribbon multiple run.

In Machine 17, full-width growth at 3 to 4 cm/min is now routine, and quality-related work will commence.

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I. INTRODUCTION

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

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

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

Also, in the five ribbon multiple run, it was demonstrated that material from such units can indeed have reasonable electronic properties, since large area (~50 cm²) cells of ~9% efficiency could be prepared from silicon ribbon grown in that experiment.

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

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

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

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

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

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

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

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

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

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

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

A. Overview

Quality studies have been initiated in the 10 cm cartridge (Machine 17) in this quarter after development of this growth system to the point where reliable and reproducible operation to obtain full-width ribbon at speeds of 3 to 4 cm/min has become routine. Initial results show SPV diffusion lengths of 10 to 30 μm for this ribbon, and solar cells in the range from 8 to 10% (AM1 and AR coated). These levels compare favorably to values achieved in earlier versions of the high speed cartridge growth systems under development for the present program. Future work is to be oriented toward examining directions in which optimization of quality in the 10 cm cartridge is to proceed.

Quality studies in the 7.5 cm cartridge (in JPL No. 1) continue to focus on the study of means by which to optimize ambient influence on growth conditions and material quality. Carbon monoxide and oxygen levels have been monitored during growth under ambient conditions typical of those for which improvements in ribbon quality have previously been achieved. Other special runs have also been carried out: from an aluminum-doped melt in the presence of ambient manipulation, with the deliberate introduction of water vapor into the growth slot, and with a cold shoe in the presence of carbon monoxide. An alternate means of preventing backstreaming of air around the ribbon growth slot, through the use of gas-tight rollers around the ribbon exit to the furnace, has been tested to compare its effectiveness with that of the gas lock in use at present.

The reproducibility of ambient changes insofar as being able to improve SPV diffusion lengths and cell efficiencies has been demonstrated for the case of reduced main zone purge rates, as cell efficiencies of over 11% continue to be realized for this material. Monitoring of CO

levels during main zone purge rate decreases has shown that CO levels arising from native furnace gases increase from threshold levels of about 10 to 20 ppm at standard operating conditions to about 500 ppm at the lowest main zone purge rate at which growth conditions remain practically viable. Increases in the SPV diffusion length are obtained already when CO concentrations reach the 50 to 100 ppm range, and it is at these levels that large grain growth also starts to appear. At moderate to heavy film cover, which generally is achieved at CO levels of 500 ppm and above, the frequency of incidence of large grain growth appears to decrease.

Ribbon grown with deliberately introduced CO₂ in the interface region has also shown to have much improved properties. Solar cells of efficiencies as high as 12.5% (AM1 and AR coated) have been achieved on this material.

B. Machine 17

Optimization of growth conditions in the 10 cm cartridge has resulted in the development of a capability for full-width growth (10.8 cm wide ribbon) at speeds of 3 to 4 cm/min. This effort included correcting several deficiencies in the growth system which had resulted in temperature imbalances and insufficient power availability, as well as the evaluation of several die-top heater, die design and die-top shield combinations for purposes of improving ease of spreading and stability in growth of full-width ribbon. This work was completed before the system was cleaned up for quality work. After the furnace interior was thoroughly cleaned and the 10 cm cartridge rebuilt with baked-out and cleaned components, operation in a clean mode was started with run 17-062. Nine runs have been made with this clean cartridge. The initial results from these runs are discussed in Section III.

Each run generally yields 3 to 4 meters of ribbon and the crucible is always emptied. About 80 to 90% of ribbon is full-width. Some difficulty in scribing has been experienced because of the lack of a suitable scribing facility. The thinnest (~0.02 cm) ribbon has been particularly difficult to scribe across the full width even though it was reasonably flat (less than 0.08 cm deviation from flatness for the most part). However, this problem has been gradually alleviated by improvements in the growth conditions to yield more uniform thickness and flatter ribbon. Growth speeds were intentionally kept to the range of

2.5 to 3.5 cm/min initially to increase the yield of available ribbon for quality studies and cell fabrication purposes.

Future work will focus on additional optimization and improvements in the growth system and efforts to increase the yield of ribbon at higher growth speeds. The quality work will be extended to include operation of a 10 cm cartridge without a cold shoe to facilitate a comparison of the effects of ambient manipulation on growth conditions and material quality with and without cold shoes in the growth system.

C. Machine 18

Experiments have been continued in this reporting period to better characterize the growth system ambient over the range of operating conditions which have been associated with the onset of film formation, large grain growth, and material quality improvements. These experiments are summarized in Table I. The main emphasis has been on attempting to reproduce the high performance ribbon as achieved in earlier runs at reduced main zone purge rates. Carbon monoxide and oxygen levels were measured in a number of runs. The results of these and other experiments are discussed in more detail below.

The carbon dioxide concentration in gas jets exiting in the growth slot at which the first trace of visible ribbon film appears was determined in run 18-177. A 1% CO₂ in argon tank mixture was further diluted in a mixer to obtain effective CO₂ concentrations from zero up to 1000 ppm. Visible films first began to appear at a mixer CO₂ concentration of about 200 ppm. The first stains were preferentially located along the ribbon center line, opposite the exits of the gas jets. The film pattern was very irregular and tended to reflect the ribbon flatness profile. Because of this nonuniformity, the film cover did not fully extend to the ribbon edges until CO₂ mixer concentrations of about 600 ppm were reached.

Growth was carried out from an aluminum-doped melt in run 18-178 under various combinations of gas jet and main zone flow rates. The charge was doped to a nominal level of 3.5 Ω -cm with aluminum doped Czochralski-grown silicon. Aluminum has been shown to be useful in the study of melt transport processes in EFG of silicon ribbon.⁽¹⁾ The aluminum distribution will be very sensitive to changes in melt boundary layer conditions because of the high diffusion coefficient of aluminum, and therefore should respond to changes in interface shape and interface growth conditions resulting from ambient changes. Spreading resistance measurements will be made on this ribbon to determine whether aluminum is

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

Run No.	Speed Range (cm/min)	Length (in.)	Comments
18-177	1.8 - 2.0	5.3	Examine film formation as a function of CO ₂ concentration in gas jets.
18-178	1.8 - 2.0	6.0	Aluminum-doped melt with various main zone purge rates.
18-179	1.8 - 2.0	3.1	Repeat of baseline run conditions at high and low main zone purge rates/gas jet combinations.
18-180	1.8 - 2.0	3.8	H ₂ O introduced into growth slot.
18-181	3.0 - 3.6	5.0	Growth with cold shoe and deliberate use of carbon monoxide in cartridge.
18-182	1.8 - 2.0	6.8	Monitoring of CO concentrations in furnace for determination of threshold levels for onset of large grain growth at decreased main zone purge rates. Overnight furnace operation.
18-183	1.8 - 2.0	3.2	Repeat of run 18-182 experiments with CO level monitoring by IR spectrophotometry.
18-184	1.8 - 2.0	1.0	Four-day continuous operation to monitor furnace ambient and testing of electrolytic cell oxygen sensor developed at University of Missouri. Poor growth conditions after second day.
18-185	1.8 - 2.0	5.3	Repeat of run 18-150 to reproduce optimum ribbon quality under reduced main zone purge rate conditions.
18-186	1.6 - 2.4	3.3	Repeat of run 18-185.
18-187	1.8 - 2.3	4.0	First test of gas-tight rollers for control of gas leaks at cartridge exit.
18-188	1.8 - 2.0	2.9	Additional experimentation with gas-tight rollers.
18-189A	-	-	Main zone power failure due to overheated power studs.
18-189B	1.8 - 2.0	4.0	First attempt at gas manipulation above bulk melt; fails due to quartz tube breakage.
18-190	1.6 - 2.2	3.6	Repeat of 18-189B with CO ₂ introduced to region between crucible and cartridge floor. Undoped melt.

useful as a tracer to give information on the effect of the ambient on interface melt conditions.

In order to check whether any contamination of the growth system had occurred as a result of use of the aluminum-doped charge, a baseline run, 18-179, was made to monitor as-grown material levels at high and low main zone purge rates. An additional combination of main zone and gas jet flow rates was also investigated: the main zone was turned completely off and film cover was studied as a function of the gas jet argon flow rate. It was found that the ribbon surface could be maintained essentially film free at rates as low as 1 ℓ /min in this situation.

One run, 18-180, was devoted to the investigation of the influence of H_2O on growth conditions and ribbon quality. Water vapor was introduced into the growth slot via the gas jets by passing the argon supply to the jets through a bubbler. The latter consisted of a fritted glass tube submerged in water in a conventional trap arrangement. Flow rates of 100 to 200 cc/min were found to lead to visible film formation on the ribbon. If it is assumed that the argon is saturated with water vapor at its partial pressure at room temperature ($20^\circ C$) in passing through the bubbler, this would yield about 17 mm of H_2O in the argon entering the furnace. Growth conditions were reasonable throughout the time the gas jets were on, and no specific growth-related difficulties were attributed to the presence of the water vapor. SiC particle densities were generally low, although the degree of suppression of SiC growth observed with other ambients was not achieved. The main zone argon purge rate was maintained at 10 ℓ /min throughout the time the gas jets were being used. This was the only combination of gas flows utilized because the run was terminated prematurely due to excessive water entering the gas jet line. This occurred when the jet argon flow rate was inadvertently turned up to high: water drops were swept into the gas line and the die top was immediately covered with deposits and growth was no longer possible. The exposure of the cartridge to the water vapor resulted in heavy SiO_x deposits on many components, and the cartridge was no longer usable after this run.

A single run (18-181) was made with the cartridge with the cold shoe in conjunction with deliberate CO introduction into the neighborhood of the growth interface. The CO was introduced via a molybdenum gas flow tube extending into a corner of the cartridge, originally used to improve cartridge atmosphere control, as described in a previous report.⁽²⁾ A 50% CO in argon tank mixture was further diluted in a mixer to produce CO

concentrations of 1000 to 5000 ppm in the gas entering the cartridge. With the main zone purge rate off, this range of CO concentrations resulted in moderate to heavy film being formed on the ribbon. Ribbon was grown first with just argon in the cartridge, then with various concentrations of CO. Growth conditions were reasonable throughout the run, and die-top SiC growth suppression appeared to be comparable to that experienced in runs without the cold shoe under similar ambient conditions.

The concentration levels of CO were monitored in the cartridge growth slot as a function of the main zone purge rate in both runs 18-182 and 18-183. A Kitagawa CO detector tube and cell* were used to sample the cartridge ambient through the same tubes in the gas jet configuration which have been used to introduce gas to the growth interface region.

The detector registered CO concentrations from 5 to 15 ppm under standard main zone argon flow conditions of 10 ℓ /min. Significant deviations out of this range did not occur until the main zone purge rate dropped below 5 ℓ /min, as shown in Fig. 1. The measurements were reported in run 18-183 in parallel with IR spectrophotometer monitoring of the CO peak in a standard gas detection cell. The IR data is calibrated on the basis of ASTM standards, which fix the lower limit of detection for CO in the associated cell at about 30 ppm. With this calibration, the IR results fall considerably above those obtained with the Kitagawa cell, but all sets of data show consistent increases in CO levels over a range of decreasing main zone purge rates from 10 ℓ /min to 1 ℓ /min.

In run 18-184, the furnace was maintained at operating temperature continuously for four days in order to examine ambient conditions under longer term operating conditions than encountered in the one-day runs typical of the JPL No. 1 operational mode. An electrolytic cell oxygen sensor was installed prior to this run by Drs. D. Ownby and H. Romero and kept in operation throughout. The details of the findings will appear in their reports to JPL. Measurements of both the O and CO levels were made through the gas jet inlets in the growth slot region. Oxygen was also detected in the incoming argon used to purge the furnace, thus pointing to the purge gas as an additional source of oxygen in the furnace. The oxygen introduced in this way would be expected to react with

*Kitagawa detector tube (Type 1065) and Kitagawa cell (Model No. 8014-400), manufactured by Matheson, Lyndhurst, New Jersey.

Fig. 1. Measured CO levels in JPL No. 1 as a function of main zone purge rate.

the plentiful supply of graphite in the furnace components to form CO, thus acting as a continuous supply of this gas. No significant changes in the CO levels were detected during overnight operation at a given purge rate, indicating steady-state for the CO is probably established over times of the order of a few hours after a change in purge rate is made.

A more effective means of control of backstreaming air to the growth interface was tested in runs 18-187 and 18-188 with the installation of a set of gas-tight rollers at the exit of the cartridge growth slot. The rollers were driven by a separate motor which was temporarily synchronized to the stroke puller motor speed. The purpose of the test was to evaluate this mode of sealing the ribbon exit in order that such gas-tight rollers could eventually be incorporated into a continuous belt puller as the lower of the two sets of rollers generally used in these pullers.

Initial attempts to synchronize the roller motor with that of the stroke puller were not entirely successful because the latter tended to run irregularly in certain regions of its stroke. Frequent freezes were encountered as a result. In addition, due to the absence of a sufficiently narrow growth slot, the gas-tight rollers tended at times to deflect the ribbon very abruptly in regions where it deviated from flatness, thus causing additional freezes. Initial adjustments of the various furnace purge gas rates showed that the rollers were sufficiently tight to allow operation at very low total purge rates, of the order of a few liters per minute, as backstreaming of air appeared to be totally suppressed with this arrangement. However, the presently used designs were not satisfactory, and the concept thus needs further evaluation.

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

A. Overview

The developmental work done in this quarter on the 10 cm growth cartridge consisted primarily of changes to accommodate the future use of reactive gases as an ambient to the meniscus and ribbon. These component changes, particularly the substitution of a graphite die top radiation shield for the previous one of molybdenum, degraded the growth performance of the cartridge sufficiently to require re-optimization of the die heaters and cold shoes, a process which is still underway.

In addition to this developmental work, most of the remaining equipment to operate the furnace in multiple (three 10 cm ribbon) mode was assembled by project personnel. The demonstration of multiple growth which was scheduled to have taken place by year's end has been delayed until shortly into 1980.

B. Cartridge Component Changes

Experimental work currently ongoing in single station Furnace No. 1 strongly suggests that photovoltaic quality of the ribbon is improved both by reduction of the gas outflow rate through the cartridge from the main zone, and by the controlled addition of oxygen-bearing gases to the ribbon's environment. In preparation for repeating these experiments in the multiple 10 cm system, three changes were made to the cartridge components.

In order to reduce the amount of molybdenum available to react with oxygen-bearing gases and possibly contaminate the melt and/or ribbon surface, the die-top radiation shield material was changed to graphite. Following this substitution, the only non-graphite components in the hot portion of the cartridge are the six 5 mm diameter heating element feed

bars of molybdenum, the tungsten-rhenium thermocouple, and the silica thermocouple insulator. The ramifications of this change of the die-top shield material are further discussed below.

A set of gas passages was designed into the cartridge to allow introduction of a gas into the channel between the linear cooling plates, as in the cartridge used in Furnace No. 1. These passages are an improvement over the experimental setup used in that furnace insofar as the gas issues from six jets spaced evenly across the face of each linear cooling plate, and the connecting hardware is durable and well integrated into the cartridge design.

A gas lock was also designed for the cartridge exit slot to prevent backstreaming of air under conditions of low main zone purge rate. These three changes are shown in Fig. 2.

C. Summary of Growth Runs

The ten single-cartridge developmental runs made in this quarter are listed in Table II. Numbers 204, 208, 210, and 212 entailed removal of the cartridge for modification or part replacement, and reinsertion. Table III illustrates the effects of changing to a graphite die-top radiation shield; the growth rate and duration of the 15-run segments which produced significant quantities of full-width ribbon in runs 198 through 205 (moly shield) and 206 to 207 (graphite shield) are listed. The reduced rate and poorer stability are due to the increased temperature of the radiative environment of the ribbon. Changing the standard after-heater temperature setting to a higher value at nearly the same time as the change in shield material was made also contributed to these effects.

The average duration of growth segments can only be taken as a very rough indicator of the relative stability of different configurations, since the durations of the individual segments are affected by factors which are not controlled or reported in run notes. However, the temperature of the die heater thermocouple observed in these runs provides a quantitative measurement of a condition related to stability of growth. As the data of Table IV show, the die-heater thermocouple was consistently colder by about 35°C with the graphite die shield in use. The thermocouple is a thermal analogue of the body of the die, and this lower temperature is believed to indicate a smaller temperature gradient through the die tip and silicon meniscus.

An attempt was made in runs 208b, 209, and 210a to correct for the lessened gradient by using cold shoes with larger surfaces facing the

Fig. 2. Ten cm ribbon growth cartridge. Recent modifications denoted by *.

Table II. Summary of Growth Runs.

Run No.	S = Slot Thickness (cm) D = Displacement (cm) B = End Stabilizing Feature* C = Capillary Configuration**				Die Shield Material	Cold Shoe Thickness (cm)	End Heater Length (cm)	Face Heater Type***	Quality Full Width (in)	Stability	Comments
	S	D	B	C							
204a	.038	.015	0	SC	C	.28	2.6	P	0	poor	Slow growth, difficult spreading. Seed ribbons broke repeatedly.
204b	.038	.015	0	SC	Mo	.28	2.8	P	0	poor	Improper silicon feeding due to gas bubble in die.
205	.038	.015	B	2P	Mo	.28	2.8	P	6.1	good	
206	.038	.015	B	2P	C	.28	2.8	P	12.2	good	
207	.038	.015	B	2P	C	.28	2.8	P	3.0	fair	
208a	.038	.008	B	SC	C	.29	1.2	P	0	poor	Experimented with bulb dimensions. Cartridge withdrawn because gas bubble was suspected in die.
208b	.038	.015	B	SC	C	.43	1.2	P	0	-	Thicker cold shoes installed. No growth possible, due to broken seed.
209	.038	.015	B	2P	C	.43	1.2	P	0	poor	Broken seeds and die/floor flood.
210a	.038	.011	B	2P	C	.43	2.8	P	0	poor	Higher melt level. Irregular die-top isotherm, cause not determined.
210b	.038	.013	B	2P	C	.28	2.3	P	0	-	Crucible failure and major flood.
211	.038	.013	B	2P	C	.28	2.3	P	0.8	poor	Run terminated by broken ribbon.
212a	.038	.015	B	2P	C	.28	2.3	P	1.4	fair	Lateral thermal asymmetry hindered stability.
212b	.038	.015	B	2P	C	.28	2.3	S	1.9	fair	Changed face heater. Experimented with thermal effects of melt replenisher.
213	.038	.015	B	2P	C	.28	1.2	S	2.1	fair	Changed end heaters. Thickness profile slightly better.

*End stabilizing feature: 0 - none; B - bulbs.

**Capillary configuration: SC - one piece die, saw cut capillary; 2P - two-piece die.

***Face heater type: P - profiles (thin central portion); S - straight (uniform thickness).

Table III. Growth Rate and Stability vs. Die Shield Material.

Run No.	Die Shield Material	Afterheater Setpoint (mV)	Segment No.	Duration (mins)	Growth Rate (cm/min)
198	Mo	19.0	2	114	3.43
	Mo	19.0	4	120	3.30
199	Mo	19.0	2	125	3.18
200	Mo	19.0	2	103	3.43
	Mo	19.0	3	75	3.05
201	Mo	19.0	1	30	3.35
205	Mo	19.5	2	60	3.15
Average				89.6	3.270
206	C	19.5	1	30	2.79
	C	19.5	2	60	3.30
	C	19.5	4	15	2.92
	C	19.5	8	85	3.18
207	C	19.5	1	30	2.92
	C	19.5	2	36	3.05
	C	19.5	5	25	2.79
	C	19.5	7	35	2.87
Average				39.5	2.978

Table IV. Relative Die Heater Thermocouple Temperature vs. Die Shield Material.

Run No.	Shield Material	Relative Main Zone Temp. ($^{\circ}\text{C}$)	Relative Afterheater Temp. ($^{\circ}\text{C}$)	Relative Die Heater TC Temp. ($^{\circ}\text{C}$)
200 (Baseline)	Mo	0	0	0
198	Mo	0	0	- 2.8
205	Mo	+14	+30	- 2.8
206a	C	0	+30	-41.8
206b	C	+11	+30	-41.8
207	C	+56	+30	-34.8

ribbon. In the first two of these instances, seed ribbons broke in the region of the cold shoe, indicating a higher level of stress than with the thinner shoes.

In the third instance, the meniscus height profile was too irregular for satisfactory growth, for unexplained reasons. Use of the thicker cold shoes was discontinued until such time as the function of the cold shoe can be studied in greater detail.

The purpose of runs 211, 212, and 213 was to re-establish conditions for stable, full-width growth. The face heater/end heater configuration was changed, as indicated in the table, to obtain more uniform ribbon thickness profile at the higher end of the growth rate range attainable with this cold shoe/shield combination under ideal conditions (about 3.3 cm/minute).

Although the linear cooling plates with gas passages were in place from run 209 onward, the only use made of them was to demonstrate the possibility of growing film-free ribbon with very low main zone purge flow (e.g., 5 liters/minute).

In runs 209 and 210, the silicon level in the crucible was raised by 0.6 cm to reduce the height of capillary rise to the die tip from 4.1 to 3.5 cm and hence improve stability. The increased melt depth caused the crucible to break from freezing-over of the top surface when the cartridge was removed in the middle of run 210. The crucible failure and flood became apparent soon after the cartridge was reinserted.

D. Equipment Construction and Modification

The first unit of the pulling mechanism designed for 10 cm ribbon and briefly described in the Annual Report was assembled and is ready for use in the next growth run, No. 214. It appears to work well, and two additional units will be built in January. Three new cartridges were also constructed. Initial assembly of cartridge components includes a number of brazing, bending, epoxy cementing, and secondary machining steps. Two new cartridge power supplies were assembled. The melt feeding unit was modified to improve the cooling of components in its upper portions. Finally, one of the cartridge power supplies was outfitted with closed-loop RMS current controllers for the end heaters. These are intended to regulate end heater power against power-line voltage variations.

E. Multiple Growth Demonstration Runs

The demonstration of simultaneous growth of three 10 cm ribbons for two hours at 3.5 cm/minute, which was to have taken place by the end of 1979, has been delayed for two primary reasons. First is the unexpected loss of stability and growth rate capability attendant to the substitution of die shield material and the low productivity of the attempts made to regain that performance. This low productivity was in part due to accidents (seed breakage, silicon floods). However, it also indicates that factors affecting growth rate and stability need to be studied more systematically in the context of this particular piece of hardware.

A second cause of postponement of these runs has been vendor delays. In particular, the spare heating elements for the furnace ordered in September had not been received by the end of December. The furnace was inoperable after the flood of run 210 while the heating elements were being etched clean of silicon, and again when one was broken by violent break-up of the crucible after run 213.

F. Automatic Controls Task

Progress in this task during the fourth quarter has consisted of completion and initial testing of the prototype video analysis system designed at Mobil Tyco. The previously standing plan to further study ribbon dynamic response and to implement closed-loop control of growth on Furnace 17 was altered. This work will now be performed using Furnace 3A after multiple 10 cm ribbon growth has been demonstrated.

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IV. CELL AND MATERIALS CHARACTERIZATION

A. Cell Characterization by C.T. Ho

1. Overview

During this quarter, we have concentrated our efforts on demonstrating the feasibility of obtaining a conversion efficiency $\geq 12\%$ in a minimum area of a 4 cm^2 ribbon solar cell made from the resistance furnace-grown material. It will be shown that the goal has been met by the use of the ribbon material grown from the CO_2 gas ambient experiment of Furnace 1, together with the standard PH_3 diffusion procedures. The strong light enhancement effect of the bulk diffusion in the gas treated material is believed to play an important role in obtaining the high efficiency demonstration goal.

Three fabrication runs have been made for the demonstration cell. We shall discuss each run separately.

a. Run HE-1

In this run, we selected the ribbon material from a previous, reduced ambient, growth run, No. 18-150. The as-grown ribbons have an average SPV bulk diffusion length of $40 \text{ }\mu\text{m}$. The cell blanks were cut into $2.5 \times 10 \text{ cm}^2$. During the cell fabrication, we added a layer of $\sim 2000 \text{ }\text{\AA}$ undoped CVD oxide on the back side of the cell before the high temperature (1025°C) drive-in to form the N^+ junction. The purpose for this extra process was to protect the cell sample from possible contamination during the drive-in. The metal evaporation mask had a finer grid and finger pattern than our standard $5.5 \times 10 \text{ cm}^2$ metallization mask. The overall metal coverage area for this HE series run was 8%. The finished cells were then randomly cut into $\sim 6 \text{ cm}^2$ before the measurements. The results for the top ten higher output cells are summarized in Table V.

Table V. Summary of the Solar Cell Data for Cell Run HE-1. The Cells are Fabricated from the High Temperature (1025°C) CVD Diffusion Process. Ribbon Material is from Growth Run 18-150.

100 mW/cm²; ELH Light, 28°C; AR Coated; Area = 6 cm²

Cell No.	J _{sc} (mA/cm ²)	V _{oc} (Volt)	FF	η (%)
1	26.7	.569	.726	11.0
2	27.1	.574	.747	11.6
3	27.3	.569	.706	11.0
4	27.2	.569	.756	11.7
5	27.2	.568	.717	11.1
6	27.7	.578	.694	11.1
7	26.8	.570	.722	11.0
8	27.1	.568	.745	11.5
9	27.2	.569	.725	11.2
10	26.9	.571	.732	11.2
Average	(27.12)	(.571)	(.727)	(11.24)

The highest conversion efficiency achieved in this run was 11.7%. It appears that the photovoltaic output was still limited by the short circuit density of $\approx 27 \text{ mA/cm}^2$. The bulk diffusion lengths of the typical cell were determined to be ranging from 32 to 41 μm . Thus, there was no serious degradation in the diffusion length of the ribbon after the cell processings.

b. Run HE-2

In this run, we selected the ribbon material grown from run 18-185, which was another growth run with reduced ambient condition. The average diffusion length of the as-grown ribbon was 42.5 μm . During the fabrication process, we have tried to optimize the cell performance by varying the diffusion temperature and kept the drive-in time (40 minutes) constant. Three temperatures, 1000°C, 1025°C, and 1050°C, were chosen for the diffusion. The remaining procedures were essentially the same as those in the previous run, HE-1.

As shown in Table VI, some definite trends can be observed among the three diffusion groups. First of all, there is a reduction in J_{sc} as the diffusion temperature increases. We construe this to be primarily due to the junction deepening rather than to a loss in bulk diffusion length, since we have already shown experimentally that there is negligible degradation after the doped oxide source diffusion over this temperature range.⁽³⁾ The increase of V_{oc} with the higher temperature process can be interpreted in several ways: (i) there is an increase of the minority carrier lifetime in the CVD diffused layer, (ii) there is a reduction in effective surface recombination, or (iii) there is an increase of the effective doping concentration in the N^+ diffused layer, as the result of deepening the junction. All these possibilities will cause a decrease in the reverse saturation current density at the front surface layer, and thus yield higher V_{oc} .⁽⁴⁾ Nevertheless, the highest conversion efficiency for this run was again 11.7% from the 1050°C diffusion temperature group. It still falls short of the 12% goal.

c. Run HE-3

In the past, we have noted that the cells made from ribbon grown from quartz crucibles exhibited strong light enhancement effects in the diffusion length after the PH_3 diffusion process. We strongly suspect that the existence of oxygen in a ribbon might promote formation of

Table VI. Summary of the Solar Cell Data for Cell Run HE-2. The Cells are Fabricated from 1000°C, 1025°C, and 1050°C CVD Diffusion Temperature. Ribbon Material is from Growth Run 18-185.

100 mW/cm²; ELH Light, 28°C; Area $\approx$ 14 cm²

Diffusion Temp. (°C)	Cell No.	J _{sc} (mA/cm ²)	V _{oc} (Volt)	FF	η (%)	Notes
1000	1	19.3	.539	.640	6.7	No AR
	2	18.6	.533	.608	6.0	
	3	19.0	.540	.603	6.2	
	4	18.9	.542	.586	6.0	
	5	18.6	.532	.600	5.9	
	6	19.2	.538	.613	6.3	
	7	19.5	.540	.618	6.5	
	8	19.7	.558	.701	7.7	
	8A	27.1	.569	.664	10.2	AR Coated
1025	1	18.2	.529	.678	6.5	No AR
	2	19.6	.562	.740	8.1	
	3	18.7	.545	.717	7.3	
	4	19.2	.552	.755	8.0	
	5	18.5	.544	.714	7.2	
	6	19.3	.549	.701	7.4	
	2A	27.5	.572	.669	10.5	AR Coated
	3A	26.8	.564	.601	9.1	
	4A	27.1	.562	.731	11.1	

Table VI (Continued)

Diffusion Temp. ($^{\circ}\text{C}$)	Cell No.	J_{sc} (mA/cm 2)	V_{oc} (Volt)	FF	η (%)	Notes
1050	1	18.7	.548	.728	7.5	No AR
	2	18.6	.545	.658	6.7	
	3	18.0	.548	.758	7.5	
	4	18.1	.550	.771	7.7	
	5	17.6	.542	.690	6.6	
	6	18.7	.552	.723	7.5	
	7	18.9	.558	.770	8.1	
	8	18.3	.547	.772	7.7	
	9	18.8	.551	.766	7.9	
	10	19.3	.557	.763	8.2	
	11	19.0	.556	.781	8.3	
	12	17.1	.534	.733	6.7	
	13	18.6	.546	.767	7.8	
	14	19.2	.561	.757	8.1	
	15	18.8	.562	.766	8.1	
	1A	26.4	.560	.717	10.6	AR Coated
	3A	25.5	.561	.749	10.7	
	4A	25.7	.564	.766	11.1	
	6A	25.5	.564	.704	10.1	
	7A	26.7	.569	.770	11.7	
	8A	25.8	.559	.752	10.8	
	10A	27.0	.569	.753	11.6	
	11A	26.8	.569	.767	11.7	
	13A	26.3	.560	.745	11.0	
	14A	26.3	.575	.741	11.2	
	15A	25.9	.573	.734	10.9	

"donor states" and thus contribute to minimize recombination activity under illuminations. In run 18-172, which was grown with CO_2 gas introduced into the system, we have detected an interstitial oxygen concentration about $4.5 \times 10^{17} \text{ cm}^{-2}$ by IR absorption measurement. It also has an averaged SPV diffusion length of 46 μm . Thus, we selected this ribbon material and employed the PH_3 diffusion process for the cell fabrication in order to benefit from the bulk diffusion length enhancement phenomenon to achieve the high efficiency goal.

The results of cell data are shown in Table VII. These were three cells with area $> 14 \text{ cm}^2$ yielding a conversion efficiency in excess of the 12% goal. Cell No. 9 was partially broken during the fabrication process but yielded the highest efficiency of 12.3%. The cells of this run had an average $J_{\text{sc}} > 28 \text{ mA/cm}^2$, higher than any previous CVD processed run. The diffusion length vs. intensity measurement (Fig. 3) showed a relatively strong enhancement effect.

Thus, we have demonstrated that it is feasible to obtain a solar cell $> 12\%$ conversion efficiency from the resistance furnace-grown material. It requires the combination of oxygen containing and/or long diffusion length ribbon material, as well as a proper choice of diffusion and/or heat treatment procedure to meet the high efficiency goal.

B. Materials Characterization by J.F. Long

1. Overview

In Furnace No. 1, efforts have continued to improve material quality via manipulation of the furnace ambient. Reduction of main zone argon purge rate and the introduction of various gaseous species have been attempted. Under certain conditions, reproducible improvement in minority carrier diffusion lengths has been found.

Furnace No. 3A has operated in a developmental mode, and characterization data have been generated on only one run.

Furnace No. 17 has embarked upon a series of clean, 10 cm wide runs with a cold shoe for high speed growth. Various die modifications were made. Results are thus far encouraging.

2. Furnace No. 1 (18)

The series of runs undertaken this quarter focused on the furnace ambient, including reduced main zone purge rate and the introduction of CO and CO_2 via the interfacial region gas jets.

Table VII. Summary of the Solar Cell Data for Cell Run HE-3. The Cells are Fabricated from Standard PH₃ Diffusion Process. Ribbon Material is from Growth Run 18-172.

100 mW/cm²; ELH Light, 28°C; AR Coated

Cell No.	Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (Volt)	FF	η (%)
1	14.3	28.5	.578	.701	11.6
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	.582	.769	12.5

Fig. 3. Bulk diffusion length, L_n , enhancement characteristics for run HE-3.

Two samples from run 18-177 were examined, one with normal main zone purge and no gas jet, and one involving the introduction of CO_2 via the jet. The difference in minority carrier diffusion length averages for these samples (19.2 μm vs. 29.9 μm) reflects the differences seen in prior CO_2 runs, although in this case, the overall level is somewhat depressed.

Run 18-178 was aluminum-doped to a calculated melt resistivity of 3.5 $\Omega\text{-cm}$. Four-point probe profiles indicate an average ribbon resistivity of 9.9 $\Omega\text{-cm}$ (Fig. 4). Note that the level is fairly constant across the width of each sample (although the outermost measurements are taken a full 5 to 7 mm from each edge). Both of the samples on which a gas jet impinged display dips in the resistivity near the center (1L and 4K). SPV diffusion length averages produce no clear indication of the effects of the various changes made, though it should be noted that the average diffusion length is high (42.3 μm).

Sample No.	Gas Flow Conditions	$\bar{L}_D$ (μm)
18-178-1H	melt zone high; no jet	45.5
18-178-1L	melt zone high; AR jet	30.7
18-178-4K	melt zone high; CO_2 jet	44.9
18-178-5H	melt zone low; no jet	52.4

Two samples were examined from run 18-179, in which various levels of purge and argon jet flow were tried. These two samples represent full standard main zone flow, and no main zone with low argon jet flow. The diffusion length averages (25.5 μm and 39.9 μm , respectively) again suggest the material quality improvement which has been observed under these circumstances in the past.

Run 18-180 involved the introduction of H_2O in varying concentrations into the furnace ambient. No trend was found in minority carrier diffusion length as a function of water concentration. The average for the run was somewhat low (31.5 μm).

Run 18-181 involved the reintroduction of the cold shoe into the cartridge. Additionally, carbon monoxide was introduced into the main zone ambient at various levels. The run average diffusion length was found to be uniformly depressed (16.6 μm). This may well be due to the introduction of contaminants into the system with the new cold shoe. No trend in diffusion length as a function of CO concentration was found.

Fig. 4. Spatial resistivity profile for Al-doped run 18-178.

Run 18-182 was the first run following a general furnace clean-up procedure. The diffusion lengths of all three samples were low, with no effect of main zone flow rate observed ($\bar{L}_D = 22.0 \mu\text{m}$). Run 18-183 repeated the attempt. The main zone flow rates and diffusion length averages for the three samples examined were:

Sample No.	Main Zone Flow (ℓ/min)	$\bar{L}_D$ (μm)
18-183-2I	3	23.3
18-183-3F	2	42.8
18-183-3J	1	41.4

Again, it appears that the lower rates are more beneficial.

In run 18-185, the ribbon was allowed to grow in "steady state" conditions with a main zone flow rate of 3 to 4 ℓ/min . The average diffusion length 42.5 is again high, with a very tight spread of values for each sample (40.8, 44.9, and 41.7 μm).

Run 18-186 experimented with low flow rates as in 18-185. The results are presented below. The last sample was deliberately grown at a slower speed and was thicker than the other samples. This seems to point to a large degree of sensitivity to growth parameters which can now override the beneficial aspects of ambient improvements.

Sample No.	Main Zone Flow (ℓ/min)	$\bar{L}_D$ (μm)
18-186-1J	10	27.8
18-186-2G	2 - 3	45.4
18-186-6C	2 - 3	17.2

Runs 18-187 to -190 were all main zone reduction experiments which also served to test an experimental gas lock roller setup (see Section II). None of these runs exhibited a large spread of diffusion length sample averages, regardless of main zone flow rate. The run averages were 34.4, 43.4, and 33.2 μm , respectively.

Finally, 18-190 involved the introduction of CO_2 via a gas jet onto the surface of the melt. Table VIII summarizes the data, comparing cases of CO_2 introduction at the meniscus to that above the melt.

3. Furnace No. 17

The series of runs examined this quarter involved an attempt to establish baseline clean growth conditions for the 10 cm system. Only

Table VIII. Summary of Samples from Run 18-190.

Sample No.	Gas Flow Conditions			$\bar{L}_D$ (μm)
	Main Zone (ℓ/min)	CO_2 Flow (cc/min)	Onto	
18-190-1E	3	0	-	28.9
18-190-1M	3	300	melt	42.2
18-190-3K	3	100	melt	38.2
18-190-4G	10	300	interface	41.6
18-190-4L	3	300	interface	37.8

Note that the " CO_2 off" case (28.9 μm) is lower than the " CO_2 on" cases ($\overline{40.0}$ μm), and that no difference is observed between introduction of CO_2 onto the melt and onto the interface.

17-062 was grown without a cold shoe; displaced dies were used twice (17-067 and 17-069). A ribbon thickness gradient from side to side appeared, which was traced to inhomogeneities caused by the cold shoes, and which persisted from 17-063 to 17-067.

From run 17-062 no full-width material survived the scribing procedure; hence, several small samples were selected randomly and examined. Minority carrier diffusion lengths were found to be reasonably high ($\bar{L}_D = 24.5 \mu\text{m}$) for a first attempt at clean growth, but again it must be remembered that this does not necessarily reflect the ribbon quality over its entire width.

Runs 17-063 and 17-064 both utilized a cold shoe. In each case, difficulty was experienced with the die top temperature profile, and both runs produced material which was considerably thicker to one side. Both runs show striking correlation between ribbon thickness and minority carrier diffusion length. In each case, the straight line fit (via the method of least squares) is with a confidence of $> 99\%$. The average $\bar{L}_D$ for 17-061 was $15.5 \mu\text{m}$. The lower average may be a result of the introduction of the cold shoe, though subsequent runs are again higher. Run 17-064 averaged $30.3 \mu\text{m}$. Three samples were examined from regions of the ribbon fairly close to each other. Again, the asymmetric thickness problem occurred (and persisted throughout the run), and again a striking correlation was found between $\bar{L}_D$ and t . Figure 5 is a plot of all three samples examined, with a fit to a least squares straight line of $> 99.9\%$ certainty.

A single sample from 17-065 was examined which again possessed this systematic thickness variation. Again, a least squares straight line relationship of $> 99\%$ certainty was found. The sample $\bar{L}_D$ was $28.5 \mu\text{m}$. A clear correlation was also found for 17-066 ($\bar{L}_D = 18.3 \mu\text{m}$). Run 17-067, which utilized the first displaced die attempted in clean growth in this system, also produced material of systematically varying thickness. Diffusion lengths were uniformly depressed, however ($\bar{L}_D = 10.4 \mu\text{m}$).

Runs 17-068 and 17-069 were both grown after provision had been made to correct the thickness variation problem. Run 17-068 was grown with a flat-top die, with a diffusion length average of $20.5 \mu\text{m}$. Run 17-069, the second attempt at displaced die growth, averaged $17.5 \mu\text{m}$. No correlation between thickness and $\bar{L}_D$ was found for this run.

Fig. 5. L_D vs. t , run 17-064.

4. Furnace No. 3A (16)

As Furnace 3A was operated in a developmental mode for most of this quarter, only one run was examined. Four samples from various positions in run 16-207 were examined. The diffusion length average was quite low ($\bar{L}_D = 11.8 \mu\text{m}$) and quite uniform throughout the run.

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V. REFERENCES

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4. J.G. Fossum, F.A. Lindholm, and M.A. Shibib, "The Importance of Surface Recombination and Energy-Band Gap Narrowing in p-n Junction Silicon Solar Cells," IEEE Trans. on Electronic Devices, Vol. ED-26, 1294 (1979).

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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 78,309 and cost plus fixed fee was \$2,760,414. Man hours for the fourth quarter of 1979 are 5,460 and cost plus fixed fee is \$216,096. Therefore, total cumulative man hours and cost plus fixed fee are 83,769 and \$2,976,510, respectively.

3. Engineering Drawings and Sketches Generated During the Reporting Period

See Fig. 2, page 15. Also, there are drawings in connection with Section III.D, page 18.

4. Summary of Characterization Data Generated During the Reporting Period

See Section IV. Note the achievement of 12% efficient cells from material grown in a resistance heated furnace.

5. Action Items Required by JPL

None.

6. New Technology

The effort has generated certain items of potentially "new" technology. They have been separately reported pending possible patent action.