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PHASE 2 OF THE ARRAY AUTOMATED ASSEMBLY TASK FOR
THE LOW COST SILICON SOLAR ARRAY PROJECT

Second Quarterly Report, January 1—March 31, 1978

By

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May 23, 1978

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Westinghouse R&D Center
Pittsburgh, Pennsylvania

U.S. Department of Energy

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Solar Energy

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May 23, 1978

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1. SUMMARY

Development effort has been applied in these areas during the second quarter: effects of back surface field (BSF) region diffusions, application of anti-reflection coatings and photoresist layers to web silicon cells by dipping and cell separation by laser scribing. In addition, consideration has been given to selecting appropriate adhesives for encapsulation of completed modules.

Back surface field regions for working cells have been produced by diffusion both from BBr_3 and chemical vapor deposited boron-doped glass sources. Enhanced open circuit voltage has been obtained in both cases for thin wafer and dendritic web silicon material. In the latter case, this enhancement implies electron diffusion lengths of 290 to 470 μm in the base region of the cell.

Anti-reflection and photoresist coatings have been successfully applied to dendritic web silicon ribbons by pulling from a bath. In the former case, very good film uniformity has been obtained for appropriate values of viscosity of the organometallic precursor and pull rates. These results have been successfully applied to the processing sequence originally proposed for the low cost processing of dendritic web silicon solar cells giving conversion values as high as 13% (for cells without BSF regions).

Laser scribing from the back surface of the cell has been done under conditions which allow no penetration of the laser melted region to the front junction of the cell. Under these circumstances, there is no degradation of cell performance. This method of cell separation is considered to be ready for verification of performance.

A review has been made of the properties of several organic materials as candidates for the adhesives in preparing modules with cell arrays encapsulated between sheets of glass. Room temperature curing materials have been chosen to eliminate the need for a costly and time consuming curing step.

2. INTRODUCTION

The objective of this program is to establish a process sequence and to develop key process steps for low cost manufacturing of solar arrays from dendritic web, single crystal, silicon in ribbon form. Specifically, all costs, including web silicon at \$0.17/watt, are to be considered with the aim of producing encapsulated modules of 10% conversion efficiency for a selling price of \$0.50/peak watt in 1975 dollars.

A simplified process sequence, serving as the initial basis for development work on this program, was presented earlier.* Since dendritic web silicon can be handled as long lengths of ribbon through most of the cell fabrication steps (cleaning, junction formation, AR coating and metallization) conceptual processes for continuous processing have been proposed. In most cases, the operation of a proposed process as a continuous, rather than a batch, method should lead to lower costs in materials, equipment and labor.

During the second quarter development work was performed on formation of the high/low (p+/p) junction for the back surface field regions (Section 3.1). Preliminary technical and economic evaluations were made of a dip-coating method for producing high quality anti-reflection coating layers of TiO_2 on lengths of dendritic web silicon (Section 3.2). The problem of laser damage of the collecting junction during back surface laser scribing, described in the previous quarterly report, has been satisfactorily resolved during this quarter (Section 3.3). Cells with good performance have been produced using a conceptually simple process involving dip coating application of the AR layer, photolithographic delineation of the front electrode grid pattern and preferential electroplating to reinforce the grid, as described in Section 3.4. Experimental work in support of the proof-of-operation for array encapsulation is treated in Section 3.6.

* Ref. 1, Sec. 3.1.

3. TECHNICAL RESULTS

3.1 Junction Formation

3.1.1 Calibration Studies

In the First Quarterly Report on this program, a comprehensive enumeration was made of the parameters involved on the chemical vapor deposition and annealing of boron-doped oxide films for the back surface field region.* About sixty deposition and diffusion runs were performed for calibration of conditions related to formation of the BSF region.

The following points were addressed:

1. Maximum thickness uniformity zone in the reactor for both undoped and appropriately B_2H_6 doped oxides.
2. Maximum deposition temperature for no junction formation during deposition.
3. Most appropriate deposition reactant concentrations (B_2H_6 , SiH_4 and O_2) for $\sim 2000 \text{ \AA/min}$ growth and consequent thickness control.
4. The appropriate B_2H_6 to SiH_4 ratios and the resultant deposition condition alterations.
5. The selection of the optimum B/Si ratio in the doped oxide to yield appropriate sheet resistivity and junction depth for the BSF diffusion.
6. The use of low enough temperature and short enough annealing time for BSF diffusion.
7. The minimum thicknesses of the doped and undoped (capping) deposited oxides to yield the required diffused layer.
8. The choice of the BSF diffusion annealing ambient to best avoid boron-stain formation. (2,3)
9. The thinnest possible total deposited oxide masking thickness needed during front junction formation.

* Ref. 1, Table 5, pp. 12-13.

The optimum deposition conditions arrived at are as follows:
 $T = 440^{\circ}\text{C}$, total flow = 26 l/min, B_2H_6 : $\text{SiH}_4 = 5 \text{ cc/min}: 25 \text{ cc/min}$,
 $\text{O}_2 = 1.25 \text{ l/min}$. The ratio of doped oxide thickness to capping oxide thickness is 4500 Å: 2200 Å. This is achieved for deposition times of 1.0 and 0.5 min, respectively. Annealing temperature of 1000°C for 1 hour yields R_s values of $50 \pm 20 \Omega/\text{sq.}$ and $x_j \approx 0.9 \mu$. The annealing ambient is provided by 2.5 l/min O_2 and 2.5 l/min N_2 .

3.1.2 Single Crystal Wafer Cell With and Without BSF Regions

Four sets of cells were fabricated from both 2-4 Ω -cm float zone (FZ) and 20-30 Ω -cm Czochralski (CZ) wafers. Three of the runs were made on wafers thinned to about 100 μm by etching and then provided with back surface field (BSF) regions of several depths. The most shallow back boron concentration profile ($\sim 0.3 \mu\text{m}$) was formed with a 20 min, 960°C BBr_3 diffusion. BSF regions having depths of 0.9 μm and 2.0 μm were prepared by diffusion from doped oxides at 1000°C for 1 hr. and 4 hrs. respectively. The fourth run, using 2 to 4 Ω -cm FZ material of $\sim 230 \mu\text{m}$ thickness was not provided with any BSF region. The front junction in all cases was formed by a POCl_3 diffusion of 50 min. at 825°C . The phosphorus diffusion conditions had been previously determined to produce optimum results on single crystal material. A mask design was used to give twelve cells of 1 cm^2 active area for each wafer. In this way the statistical variations in cell characteristics could be assessed readily.

Table 1 gives performance data on n^+p cells formed in the 2 to 4 Ω -cm float zone material. Part (a) of the table gives results on individual cells for a single wafer having the best average efficiency (not AR coated) for the group considered. Data for the other wafers are similar in distribution. Part (b) of Table 1 gives mean values of the performance parameters for four wafers as determined on 10 to 12 cells of each wafer.

Table 1

Performance Characteristics for Ohmic Back Contact Cells
Using Single Crystal Float Zone Silicon*

a. Individual Cells
Best Wafer

<u>Cell No.</u>	<u>J_{SC} (ma/cm²)</u>	<u>V_{OC} (mV)</u>	<u>Fill Factor</u>	<u>η (% Not AR Coated)</u>
1	20.5	549	0.71	8.5
2	20.8	549	0.70	8.4
3	20.7	545	0.69	8.2
4	20.5	547	0.73	8.7
5	22.1	550	0.73	9.4
6	22.2	550	0.71	9.2
7	22.6	548	0.72	9.4
8	22.5	549	0.73	9.6
9	22.7	551	0.74	9.7
10	22.8	550	0.73	9.6
11	22.7	545	0.69	9.1
12	22.7	549	0.73	9.7

b. Average Values
for Each Wafer

<u>Wafer No.</u>				
1	22.2	548	0.72	9.3
2	22.3	541	0.67	8.6
3	22.0	545	0.72	9.1
4	22.3	540	0.68	8.7

*P-type, 2 to 4 Ω -cm; 2 in. diameter, thickness, 230 μ m. Simulated AM1 illumination, no AR coating.

Table 2 gives individual and averaged performance parameters for BSF cells ($0.3\text{ }\mu\text{m}$ diffusion from BBr_3). These were prepared using a float zone single crystal wafer of 2 to 4 $\Omega\text{-cm}$ resistivity. The wafer had been etched to a thickness of about $100\text{ }\mu\text{m}$ prior to fabrication in order to enhance the expected effect of the back surface field region. For comparison, with a 20 to 30 $\Omega\text{-cm}$ wafer of Czochralski silicon of the same thickness, the same BSF conditions yielded the following mean parameter values for 9 cells: J_{SC} , 23.3 ma/cm^2 ; V_{OC} , 568 mV ; fill factor, 0.72; efficiency, 10.1%. Thus the back surface field processing produced similar results in the two types of material.

For the 2 to 4 $\Omega\text{-cm}$ float-zone material giving the results of Tables 1 and 2, the difference in average value of open circuit voltage for the $100\text{ }\mu\text{m}$ thick BSF cells and the $230\text{ }\mu\text{m}$ ohmic contact cells is about 34 mV . This value can be examined in terms of predicted differences for such cells as influenced by minority carrier diffusion length and cell base thickness.

Hovel⁽⁴⁾ calculates, using a simplified approach, the open circuit voltage as a function of thickness in p-base cells with and without BSF regions for electron diffusion length values of 52 and $232\text{ }\mu\text{m}$.^{*} If the difference in V_{OC} values with and without the BSF region is considered as a function of sample thickness normalized with respect to the electron diffusion length, a single curve is produced, as shown in Fig. 1.

In order to use Fig. 1 in evaluating the results given in Tables 1 and 2, it is first necessary to resolve the effect of the greater base region thickness for the ohmic contact cells. If the base material were of high lifetime ($\sim 15\text{ }\mu\text{sec}$) and long diffusion length ($\sim 232\text{ }\mu\text{m}$) then V_{OC} for a $100\text{ }\mu\text{m}$ thick cell (comparable to the BSF types of Table 2) would be about 10 mV lower than for $230\text{ }\mu\text{m}$ thick cells.^{**} Thus, the 34 mV difference in V_{OC} for the experimental cells would correspond to a 44 mV difference if the comparison were made for $100\text{ }\mu\text{m}$ thick cells.

* Ref. 4 Figs. 55 and 57

** From Ref. 4, Fig. 55.

Table 2

Performance Characteristics for Single Crystal, Float Zone Cells
Back Surface Field Regions Prepared by BBr_3 Diffusion (No AR Coatings)

J_{SC} (ma/cm^2)	V_{OC} (mV)	Fill Factor	η (%)	
22.5	575	0.72	9.8	
22.8	583	0.76	10.7	
22.6	574	0.77	10.5	
23.0	576	0.77	10.8	
22.9	575	0.76	10.6	
22.7	585	0.78	10.9	
22.8	583	0.78	11.0	
23.1	584	0.79	11.0	
22.8	583	0.77	10.9	
22.6	577	0.77	10.6	
22.3	567	0.73	9.8	
22.4	575	0.76	10.3	
22.7	578	0.76	10.6	
23.1	580	0.75	10.6	
22.9	580	0.77	10.8	
23.5	581	0.77	11.1	
21.2	577	0.68	9.0	
Mean Values	22.7	578	0.76	10.5

Fig. 1 Predicted open circuit voltage enhancement in p-base silicon cells as a function of thickness normalized to minority carrier diffusion length. (After Ref. 4)

On the other hand, if the base material were of short diffusion length ($\sim 50 \mu\text{m}$ or less), reduction of the base thickness from 230 to 100 μm would not be sufficient to cause a change in V_{OC} for the ohmic contact cell.* Thus, we can use Fig. 1 to estimate the values of (base thickness)/(electron diffusion length) for $\Delta V_{OC} = 44 \text{ mV}$ and for $\Delta V_{OC} = 34 \text{ mV}$. This gives values of 0.47 and 0.61, respectively. The corresponding estimates for L_n are 220 μm and 170 μm , with the former being preferred since it is consistent with a reduction of V_{OC} with thickness in an ohmic contact cell. The 220 μm diffusion length value corresponds to an electron lifetime of about 14 μsec in the base region.

3.1.3 Web Silicon Cells With and Without BSF Regions

Preliminary results have been obtained on the operation of back surface field regions in dendritic web silicon material. The samples reported on below were given the normal BBr_3 (20 min at 960°C) and POCl_3 (35 min at 850°C) diffusions. Table 3 gives the preliminary data on these cells.

The data given is an average of several cells within the same run. The data show strong evidence of back surface field operation with a voltage difference of 57 mV in the high resistivity web materials and a somewhat smaller difference of 40 mV for the lower resistivity case. From Fig. 1, the diffusion length values are estimated to be 288 μm and 470 μm for the 4.5 and the 15 $\Omega\text{-cm}$ material respectively. These values and the corresponding ones for electron lifetime in the base region are given in Table 4. For comparison, values of open circuit decay time constant are given in the last column of Table 4. It is interesting that these values are in approximately the same ratio as the minority carrier lifetime values inferred from the open circuit voltage enhancement for the two samples.

* Ref 4, Fig. 57

Table 3
Initial Results for Web Cells (Not AR Coated)
With and Without BSF Regions

<u>Sample</u>	<u>BSF</u>	<u>ρ (Ω-cm)</u>	<u>Thickness (μm)</u>	<u>V_{OC} (v)</u>
WEB R225	No	4-5	150	.520
WEB R225	Yes	4-5	150	.560
WEB J21	No	15	165	.493
WEB J21	Yes	15	165	.550

Table 4
Estimated Diffusion Lengths and Electron Lifetimes in
Web Silicon Cells with BSF Regions

<u>Sample</u>	<u>Thickness (μm)</u>	<u>L_n (μm)</u>	<u>τ_n (μsec)</u>	<u>τ_{OCD} (μsec)</u>
WEB R225	150	288	23	6
WEB J21	165	470	60	19

The long diffusion lengths indicated in Table 4 are obtained from web crystals that have not received any prediffusion gettering treatments. These diffusion lengths are comparable to state-of-the-art float zone and Czochralski crystals, thus indicating the suitability of web BSF cells.

3.2 Anti-Reflection Coatings by Dip Processing of Dendritic Web Silicon

Excellent antireflection coating results have been obtained by the use of specially prepared TiO_2 layers on silicon wafers. In this technique an organic precursor of TiO_2 in an alcohol solvent is applied to the silicon. The dried metallo-organic film is then baked at 400°C to produce an essentially pure, compact TiO_2 film. The refractive index of the layers, approximately 2, is ideal for the purpose and uniform layers of the required thickness have been obtained by simple spin-on techniques. Similar results have been produced by the dip coating process applied to lengths of silicon web material by pulling 30 cm lengths of the silicon web material vertically from the same solutions. Excellent uniformity ($\sim 2 \text{ \AA}$ over the 30 cm length) was achieved by the dip process at speeds of 30 cm/min ($\sim 1 \text{ ft/min}$). A preliminary economic analysis for this method of AR coating silicon-ribbon is desired to permit comparisons of its cost effectiveness vis à vis other methods for increased coupling of light into solar cells, namely vacuum depositing of AR coatings and surface texturing.

3.2.1 Process Costs

The cost of applying an AR coating to silicon web material by a continuous dip process can be treated in two parts: (1) the cost of buying maintaining and operating the equipment and (2) the cost of the consumable materials of the coating itself .

Equipment Cost. To estimate the equipment-related cost, consider a typical dipping operation designed to coat strip material analogous to silicon web. The equipment cost is in the neighborhood of \$35,000 for a one strip system and \$80,000 for a four strip system. Equipment components include payoff and take-up reels, capstan drives, the dip tank, a bake oven and the necessary machine controls for operation.

Assume:

1. A four (one) strip operation requires 0.5 (0.2) operators for loading and unloading silicon web and for general maintenance.
2. Operator cost is \$10,000/per man year.
3. Operation for 24 hrs/day, 7 days/wk, requiring four shifts.
4. Equipment cost is averaged over five years.

Under these assumptions the cost of the equipment and operators is 1.7 (2.8)¢/min/strip for the four (one) strip plant. Energy costs will increase these values to 2.0 (3.0)¢/min/strip.

Obviously, these estimates are only approximate and other fixed costs not considered must be added. These figures can serve as a basis of the cost analysis to follow.

Material Cost. The cost of the solid coating material itself is small. Use of TiO_2 as the AR layer, deposited from an organic precursor, requires a thickness of approximately $850 \text{ \AA}$ TiO_2 . A cost of \$40/3 kg for the precursor gives a corresponding cost of 43¢ for 10 m^2 . (This area is approximately that required to produce 1 KW peak power from a 10% efficient solar cell array.) The useful coverage of the AR coating has been taken as 0.4, considering the ratio of cell area to total coated area (including the edges and back of this ribbon).

Consider now the cost of the solvent (ethanol). In order to reduce the fraction of the production cost due to the equipment cost, the strips should be coated at relatively high speed. As the speed through the coating tank increases, the thickness of the liquid film drawn up by the strip increases as the square root of the velocity. Hence, at higher speeds the solution must be more dilute in order to maintain the thickness of the dried solid film at its desired level. At high speeds the main consumable expense is in the solvent rather than the solid film coating.

In simple terms

$$P = E/S + M\sqrt{S}$$

where P is the production cost (¢/ft)

E is equipment-related cost (¢/min)

S is strip speed (ft/min)

M is material cost (¢/ft/(ft/min))^{1/2}

Obviously P has a minimum value at some speed S. This optimum is $P_o = 3/2 (2EM^2)^{1/3}$ and occurs at a speed $S_o = (2E/M)^{2/3} = 3E/P_o = (2/3 P_o/M)^2$.

Figure 2 is a set of contours showing the relation between E and M for given optimized production costs (exclusive of TiO₂ cost).

Figure 3 is a plot of optimum speed, S_o, as a function of equipment-related cost, E, for various values of optimized production cost. In the interest of using a physically meaningful production volume, the optimized production cost values in both figures are given for processing 10 m² of ribbon area (1/2" wide x 2583 ft long). As noted above, such an area is required for 1 kW peak output with a 10% efficient array. Use of wider strip or cells with higher efficiency would reduce the \$/kW cost accordingly.

Figure 4 is a curve showing the production cost as a function of the strip speed both parameters being normalized to the optimized values. It shows that the cost increases only 7% for a change from 0.6 - 1.8 times the optimum speed. Hence, flexibility in the coating process is allowed with little influence on production cost.

It can be shown that the volume of solution extracted per unit width and length for this strip is

$$V = 1/3 \sqrt{2\eta S/\rho g} \text{ (cm}^3/\text{cm}^2\text{)}$$

Alcohol Cost Level of .0315 is Based on

- 1) 1/2" Wide Strip
- 2) 40% Coating Efficiency
- 3) \$2.50 Per Liter
- 4) No Recovery

Fig. 2 Optimized production cost (excluding TiO₂) contours

Fig. 3 Required optimum pull rate vs. equipment related costs

Curve 695497-A

Fig. 4 Production cost vs. pull speed

where η is the viscosity

ρ is the density

g is the acceleration constant.

Substituting values for ethyl alcohol gives

$$V = 13 \sqrt{S} \text{ microns (S in ft/min)}.$$

With 1/2" wide material and a 40% effective coating process,

$$V = 0.126 \sqrt{S} \text{ ml/ft.}$$

An assumed alcohol cost of \$2.50/litre gives the material cost

$$M = .0315 \text{ ¢/ft(ft/min)}^{1/2}$$

With this value of M and $E = 2\text{¢/min}$ the optimum speed is

$$S_o = (2E/M)^{2/3} = 25.3 \text{ ft/min}$$

and the optimum production cost is

$$P_o = 3E/S_o = \$6.13/10 \text{ m}^2 \text{ (excluding TiO}_2\text{)}.$$

In order to achieve a target cost of for example \$2/10m² with an equipment cost of 2¢/min the optimum speed must be 78 ft/min for which M must be

$$M = 2/3 P_o/S_o^{1/2} = .00585 \text{ ¢/ft(ft/min)}^{1/2}$$

$$\text{or } .00585/.0315 = 18.6\%$$

of the material cost calculated previously. This material cost can be achieved directly if the alcohol can be cheaply recovered and reused. The above implies that an 80% effective recovery is needed to attain the \$2/10 m² product cost figure. If a 90 or 95% effective recovery and

reuse could be achieved, the production cost would be respectively 1.32 or \$.83/10 m² (excluding TiO₂ cost) while the optimum pull speeds would be 117 or 186 ft/min. Such high speeds may be impractical. However, using a speed 60% of the optimum increases production cost by only 7% (see Fig. 4) which converts the above figures to 70 or 112 ft/min. A high pulling speed may well make uniform AR coatings more difficult to achieve. It also increases the path length of the bake cycle. It is anticipated that the coated strip needs 1 to 2 minutes at 400°C to sufficiently stabilize the film and achieve desired optical characteristics. Consequently, path lengths up to 200 feet long may be required, necessitating large ovens or at least complicated multipass machinery. It is clear, however, that the alcohol solvent is an important item in the total cost and alcohol recovery will be essential. (At optimum speed the material costs are twice the fixed costs.)

3.2.2 Strip Width Considerations

The above has been based on a nominal strip width of 1/2". Assuming the equipment fixed costs are not substantially affected by the use of strips somewhat wider the production cost is affected in two ways.

1. The wider the strip the less footage must be produced to cover a given area.
2. The wider the strip the greater amount of alcohol is removed per unit of strip length.

In combination, these effects cause the production cost to vary as (width)^{-1/3}; the optimized pull speed, as (width)^{1/3}. An increase in width from 1/2" to 1" therefore decreases production cost by 21% and causes a 26% increase in the optimized pull speed. Another effect of wider strip may be an improvement in the coating effectiveness from the estimated 0.4 towards 0.5 due to a decreased inactive area percentage for the wider strips, i.e., decreased edge effects. Improvements of this factor closer to 1.0 may be possible with techniques which wipe solution from the unneeded site of the strip for direct return to the tank before drying of the film can occur.

3.3 Cell Separation

The process development plan for this program defines a processing sequence for dendritic web silicon in which the material is handled in strip form, with the various process steps being of continuous rather than batch type. The final step in the continuous process is cell separation.

In the cell separation step, the dendrites must be removed from the web strip and the strip must be scribed transversely to separate the individual cells. The process which seems most attractive for cell separation is laser scribing because it is rapid, does not require mechanical support of the web and should have a high yield.

Work reported in the previous quarterly report⁽¹⁾ has shown that laser scribing can be used to remove the dendrites and to make transverse cuts across the web with high accuracy. This scribing and breaking can be accomplished with minimal loss. However, in the first several experiments the cell performance parameters were degraded by the laser scribing operation. In particular, laser scribing lowered fill factor and conversion efficiency values. It was also shown that cells scribed from the back degraded less than those scribed from the front. This degradation was tentatively identified as due to increased junction leakage current on the periphery of the cell. Chemical etching or mechanical lapping of the cell edges restored the initial cell parameter values.

A number of the back scribed cells were examined optically and with scanning electron microscopy. It was noted that, although on the average the laser spikes penetrated about 40% of the thickness of the silicon, certain areas were completely penetrated. These were areas where the scribe path had been retraced or spots at which the laser had been inadvertently permitted to dwell. This penetration would be expected to cause significant damage to the junction and thus decrease fill factor and conversion efficiency of the cell.

During this past quarter further experiments were carried out with the aim of eliminating this problem. As before, the cells were scribed at the Westinghouse Advanced Technology Laboratory in Baltimore. A KORAD KRT laser with 5000W peak power, a repetition rate of 1000 Hz and a spot diameter of 15 μm was used. The scribing speed was about 4 cm/sec.

To assure that there would be no penetration to the front, illuminated, junction the cells were scribed to a maximum penetration of 50-75 μm which required a power setting of 3500-4000 Wp. In addition care was taken that there was no retrace or laser dwell at any point on the scribe line. Figure 5 shows a scanning electron micrograph of a cell scribed in this way. As can be seen, the maximum penetration never exceeded 40% of the thickness of the cell. Some fracture lines are also evident, but these should be of no consequence to cell operation.

Thirty cell structures were scribed in this test. All had been previously prepared with back and front contacts. None had an AR coating. Seven of the samples had the dendrites attached to the edge of the cell and six samples were not mesa etched. The cells with a mesa etch were scribed within the mesa. Of the 30 cells, 8 were lost during laser set-up and calibration and four were lost due to breakage, mainly because of improper handling.

All cells were measured after scribing and breaking of the web with no further cleaning or etching processes.

The measurements made after scribing could be correlated directly with those before scribing; however, in some cases minor corrections or assumptions were required. First, when the cells were scribed within the mesa, the resultant cell area was less than 1 cm^2 , and when the cells without mesas were scribed the cell size was often greater than 1 cm^2 . In these cases, an area correction was used. Also, on the cells scribed with no mesa, data on mesa-etched cells

Fig. 5 Scanning electron micrograph of web silicon solar cell laser scribed from the back under conditions guaranteeing no penetration of the laser to the front surface.

in the same diffusion run were used as the pre-scribing reference.

Figure 6 shows the efficiency values of the cells before and after scribing. In this plot, data points to the right of the 45° line indicate cells which improved on scribing, while points to the left indicate cells which degraded on scribing. The solid dots indicate cells scribed within an existing mesa, the open circles indicate cells with no mesa. The dotted lines on either side of the 45° line indicate changes of $\pm 5\%$, which is about the accuracy of the area corrections and of the measurement. Changes of -15% to $+40\%$ are also indicated on the figure. The data obviously clusters around the 45° line. Considering only those cells for which there was individual pre-scribe data, i.e. the solid dots, 11 of the 15 cells fall within about $\pm 7\%$ of the 45° line indicating no significant change in the cell parameters. The remaining four cells in this category showed improvement from $+14\%$ to 40% . The two cells with changes of $+34$ and $+40\%$ were initially very poor with low I_{SC} , V_{OC} and fill factor. After scribing, all parameters improved with the largest effects being seen on the fill factor. This probably indicates the removal of a shunting resistance by scribing.

In cells with no previous etching, (circles in Figure 6) the initial efficiency values were taken from mesa etched cells in the same diffusion run. The spread of efficiency values is about the same as for the mesa samples. A decrease in efficiency by about 15% is indicated for one of these cells, but the initial reference value is based on a lot average and is not data for the cell in question.

The data of Fig. 6 are shown in Fig. 7 to allow convenient comparison with the earlier results.*

*Cf. Fig. 2, page 17 of Ref. 1.

Curve 695347-A

Fig. 6. Effects of controlled depth, back surface laser scribing on conversion efficiency of a group of web silicon solar cells. None were AR coated.

Fig. 7. Changes in web cell efficiency values due to limited penetration, back surface laser scribing

From this data we conclude that dendritic web solar cells can be laser scribed from the back and broken out of the web substrate without significant degradation of cell parameters. Care must be taken during the laser scribing process however, to assure that the laser does not penetrate to the front junction and cause damage there.

3.4 Processing of Web Solar Cells

As mentioned in the previous section, the development plan for this program calls for processing the web in strip form with the process steps being performed on a continuous, preferably moving, strip. Testing of such continuous processing is not feasible at this time due to lack of suitable processing equipment.

In this section we will describe a batch process, referred to as the ARRAY process, sequence that can be transferred to a continuous processing line. This ARRAY process is carried out on strips of web which are 27 cm long. The dendrites are left on the web to simplify processing and handling. A new mask design was generated for cells fabricated by this process. It is described in Section 3.5.

The process as described here assumes an input strip of silicon dendritic web with both back and front diffused surfaces. Any required oxide stripping or surface cleaning has been completed previously.

The process is as follows:

1. The diffused web strip is dipped in a liquid precursor of TiO_2 and then baked.
 - The speed of withdrawal and the viscosity of the solution must be controlled to give the proper final thickness of the AR coating. The coating thickness is also a function of the width of the web being withdrawn. At present a bake temperature of 400°C is used.
2. The strip is dipped in a positive photoresist (PR) solution (AZ-1350J) and pre-baked only.
 - The comments regarding speed and viscosity control, made above, apply here. Prebake temperature is 90°C .
3. The grid pattern of the cell is exposed in the photoresist coating the front surface of the web. The back of the strip should also be exposed to light at this time.

4. The grid pattern is developed in the front photoresist layer.
 - Regular PR developer is used. The PR layer on the back of the cell is removed at this time with the developer.
5. The grid structure is etched through the AR coating with an $\text{HCl}/\text{NH}_4\text{F}$ etch.
 - This etch will also remove the AR on the back surface of the cell.
6. Thin layers of titanium and palladium are evaporated onto the top surface.
 - For development work 1500 Å Ti and 500 Å Pd are applied by evaporation. The thicknesses of these films can be reduced to about 200 Å for production.
7. The excess metal beyond the electrode grid pattern is rejected by removing the patterned PR layer.
 - Acetone is used for PR removal.
8. The grid electrode pattern is reinforced by plating 4-5 μm of Ag.
 - The electroplating of Ag can be carried out without protecting either surface of the web strip. The silver will plate only on the metallized grid lines.
9. The back surface of the strip is metallized.
 - Both Ti/Pd/Ag and Al back metallization have been used. It is anticipated that Al or a less expensive substitute for Ag will be used in the final process.
10. The contacts are sintered, if this is required.
11. The cell is delineated by laser scribing from the back and subsequent controlled fracturing.
 - See Section 3.3 for developments in this area.

Figure 8 shows four strips prepared in the manner just described in steps 1 through 9. The individual cells are 1.6 cm x 7.0 cm in size. A fixture is now being built to allow more precise alignment of the cell patterns

Fig. 8 Twelve solar cells fabricated on strips of dendritic web silicon. Dendrites are still in place.

along the web. Figure 9 shows two 1.6 cm x 7.0 cm cells laser scribed from these strips.

During the development of this process, an experiment was run using an unfired AR coating. Figure 10 shows results of using the $\text{HCl}/\text{NH}_4\text{F}$ etch on fired and unfired films of TiO_2 . In the unfired condition (Figure 10b), the AR coating is etched back under the photoresist during the grid opening process, leaving bare silicon exposed under the PR coating. After metallization and rejection, there would be a small band of base silicon between the metallic contact and the AR coating. In the fired condition (Figure 10a) the coating is not significantly undercut.

The undercutting of the unfired AR coating may be acceptable for process simplification at some later date. Firing of the coating might be combined with contact sintering to reduce costs. The effectiveness of such a change would have to be considered in terms of the slight loss in cell performance due to reduced transmission into the silicon in the uncoated region. For the present, firing of the coating will be done prior to photolithography.

No other specific problems have arisen during this processing sequence. Techniques are being developed for handling the long strips without breaking during the various steps.

On a strip of cells fabricated by this process using a 1 cm^2 mask one - 1 cm^2 cell was removed by scribing and breaking. The properties of this cell were as follows.

Table 5
Properties of Solar Cell Produced by ARRAY Process

J_{SC} (ma/cm^2)	-----	35.60
V_{OC} (V)	-----	.534
Fill Factor	-----	.685
Efficiency (%)	-----	13.02

Fig. 9 Solar cells of 1.6 cm x 7.0 cm dimensions which have been laser scribed from dendritic web silicon.

a

b

Fig. 10. Comparison of undercutting for (a) fired and (b) unfired. TiO_2 coatings prepared from a liquid organometallic precursor.

A test apparatus is now being built for evaluation of larger sized cells ($\sim$ 1.6 cm x 7.0 cm). This includes a calibrated light source and power supply, and a hold-down jig.

As mentioned earlier, this process is economically attractive since only one PR and masking step is needed, and the requirements for acids and cleaning solutions is greatly reduced.

3.5 Mask Design

A new mask design is being used in the processing of these web strips. Figure 11 is a contact print of the electrode mask for a 2.0 x 7.0 cm cell.

The vertical bus bars, nominally 1 cm apart are perpendicular to a series of collecting grid lines with a nominal 0.20 cm spacing. The total area covered by metal is 8% and the specific resistance of the cell is 0.4 ohm-cm^2 .

One feature of this mask is that the cell can be scribed half way between any two bus bars without disturbing the basic cell design, thus cells of various areas can be obtained.

Various mask sizes from 1.6 x 4.0 cm to 5.0 x 4.0 cm are being obtained. These masks are of the same basic design with the bus bar dimensions varied to maintain a constant specific resistance. In addition a long mask - 1.6 cm x 30.0 cm is being investigated so that the strips can be masked in one operation.

Fig. 11. Contact print of the grid electrode mask for a
2.0 cm x 7.0 cm dendritic web silicon cell

3.6 Encapsulation

Encapsulation of cell arrays between sheets of glass using appropriate adhesives was considered to require proof-of-operation within the current development program. That is, an encapsulation procedure must be defined and executed to provide adequate protection to the arrays of dendritic web silicon solar cells fabricated and interconnected by the methods developed on this program.

Proof-of-operation of the encapsulation method selection involves the choice and testing of solar cell materials from the points of view of both the projected performance of the array and the applicability of the encapsulation method to a low cost, automated solar array fabrication process. The encapsulation step, as envisioned at present, would involve the use of protecting organic materials which do not require the application of heat to be set up in their final, geometrically fixed form. In this manner the use of expensive ovens and of energy would be avoided or minimized.

The tentative encapsulation approach taken involves use of RTV (room temperature vulcanizing) organic resin materials which will cure at room temperature within a length of time and under conditions compatible with a chosen automated solar cell manufacturing process. Although the curing times of most RTV resins are relatively long (0.5 to 12 hours), final curing of the encapsulant does not have to take place during the actual encapsulation process. The envisioned form of the encapsulated module is a sandwich of the solar cell array between glass plates. The array would effectively be embedded in the encapsulating medium. Adhesion to the glass and to the metal, retention of optical clarity under a variety of environmental conditions, negligible shrinkage on curing and aging, ease of application, absence of degassing, are some of the factors considered in choosing an acceptable RTV-type encapsulant.

A variety of solvent-free adhesives, obtained commercially and formulated at Westinghouse, have been screened. A type of RTV, two-part epoxy system, made by the AMICON Company, Lexington, MA, was advertised as being optically clear when set up. Catalyzed samples of

AMICON KT-11 (gel time 3 hrs, set-up in 24 hrs at RT) and KT-41 (gel time 6-7 mins, set-up in 1 hr at RT) were sandwiched between square microscope slides and allowed to cure at RT. The adhesion to the glass was excellent, but optical clarity was poor, the interposed adhesive layers exhibited a yellow cast which became darker with time. Exposure of such material to UV in a Fadeometer hastened the yellowing process greatly.

An epoxy formulation made at Westinghouse consisting of clear diglycidyl ether-bisphenol A matrix cured with triethylene tetramine (TETA) gave relatively clear layers (2-3 mils) whose optical clarity persisted after aging at 80°C and after exposure to UV at RT for several days. Shrinkage on curing appeared to be small for both types of epoxies as measured by the change of the position before and after cure of 5 mil thick 0.5" x 1" aluminum foil tabs encapsulated in the epoxies between two microscope slides.

It is well-known that epoxies in general do not possess the kind of optical properties required for optimum solar cell performance. Because of their adhesive properties these materials have, however, been used here to obtain some experience of the conditions and parameters involving the production of encapsulated solar cell arrays as described above. For example, a problem was encountered on placing silicon chips on a 2-4 mil thick layer of catalyzed but non-cured encapsulant spread on a piece of glass. Under some conditions the silicon would "float" over the surface of the liquid encapsulant before the latter sets up. This would be aggravated when the top piece of glass, with its layer of catalyzed but non-cured encapsulant, was pressed upon the silicon pieces. When this happens, the geometry of the cell array is distorted appreciably. This problem was circumvented by applying to the bottom of the chips a drop of catalyzed, fast curing epoxy. The chips were then picked up and pressed through the encapsulant layer on the lower glass cover until contact was made between the bottom part of the chip and the glass surface. Adhesion between the chips and the glass was almost immediate. When this process was used with glass substrates marked with a geometric grid of lines, no discernible displacement of the chips from their original

locations on the grids was noted even after several days at 80°C. For this placement function, epoxies are indicated, since the requirements are for fast curing, strong adhesive characteristics and not for optical properties.

4. CONCLUSIONS

4.1 Back Surface Field Studies

Back surface field regions prepared by boron diffusion have been shown to enhance the performance of p-base solar cells in both float zone and Czochralski silicon and dendritic web ribbon silicon. Diffusions have been made using a BBr_3 source as well as boron-doped, chemical vapor deposited oxide layers. The clearest results have been drawn using the former methods to produce boron concentration profiles penetrating about $0.3\text{ }\mu\text{m}$ into the silicon.

For float zone, wafer material of 2 to 4 Ωcm resistivity with a $100\text{ }\mu\text{m}$ thick base region, BSF enhancement of open circuit voltage by about 44 mV indicates an effective electron diffusion length of $220\text{ }\mu\text{m}$ in the base region.

Cells in dendritic web silicon of 4 to 5 Ωcm resistivity and $150\text{ }\mu\text{m}$ base thickness, exhibited enhancement of 40 mV by the BSF region, indicating an electron diffusion length of $288\text{ }\mu\text{m}$. For dendritic web material of 15 Ωcm resistivity and $165\text{ }\mu\text{m}$ thickness, a 57 mV increase in V_{OC} due to BSF action indicates an electron diffusion length of $470\text{ }\mu\text{m}$. These results, obtained with conventional cleaning processes and with no gettering, indicate that large values of effective electron diffusion lengths can be obtained in dendritic web silicon solar cells with BSF regions. If values comparable to those deduced for these experiments can be achieved in $100\text{ }\mu\text{m}$ thick web cells, V_{OC} enhancements of 60 to 80 mV would be realized in comparison to ohmic back contact cells.

4.2 AR Coating by Dip Application

In the application of AR coatings by a dip process a balance exists between fixed operating costs and material costs dependent upon the pull speed. For speeds near the optimum, production costs are minimized

and are little affected by variations over a factor of about 3 in the speed range, allowing great flexibility in pull speed to accommodate changes in temperature (viscosity) and solids content of the solution. The required pull rate is relatively high, in the range 50 to 100 ft/min. A significant cost in the process is that of the alcohol solvent for the coating material. Solution concentrations will be in the range 0.5-1.0% (TiO_2 /alcohol by weight). If production costs are to be brought below approximately \$6/10 m^2 , some degree of alcohol recovery is essential. A production cost of \$1.26/10 m^2 is projected for a 95% effective recovery system.

4.3 Laser Scribing

With control of the peak laser power and elimination of dwell or retrace along the cell periphery, laser penetration can be limited to less than 50% of cell thickness. This avoids penetration to the junction during back scribing.

An experiment involving scribing within the mesa of web silicon cells under the conditions discussed above revealed no reduction in efficiency for the cells tested. For 75% of the cells, post-scribing values were within $\pm 7\%$ of the initial values. The other 25% exhibited increased efficiency, presumably due to removal of portions of cell areas with lower than average photovoltaic performance.

Back surface scribing, properly done to eliminate penetration to and damage of the collecting barrier, is an acceptable means for dendrite removal and cell delineation in the processing sequence for dendritic web silicon cells.

4.4 Compatible Processing Sequence

AR coating by the dip process, photolithographic delineation of the electrode grid window in the AR coating, rejection of the regions of thin Ti and Pd external to the grid window during photoresist stripping and localized electroplating of silver have been demonstrated as a compatible sequence for cell fabrication. Only single photomasking and etching strips are required to delineate the required grid pattern.

Cells (without BSF region) of 13% conversion efficiency have been made using this process. With 15% improvement in V_{OC} due to BSF action, cells of 15% conversion efficiency should be achievable using the technology developed and demonstrated to date on this program.

5. PROGRAM STATUS

5.1 Present Status

As shown in Fig. 12, the work on this program is generally on schedule. Metallization development (Task 4) has proceeded well with the establishment of photolithographic methods for etching the AR coating and delineation of the grid pattern by rejection of unwanted Ti-Pd during stripping of photoresist. Efforts relating to proof-of-operation (Task 7) have been rearranged somewhat. Substrate preparation may be a more important area than originally anticipated. Preliminary requirements for etching have been established and utilized to date. This topic should remain active through the third quarter. Cell interconnection work has been postponed until a sufficient stock of web silicon cells is available for this work. It is estimated that this work will be completed by the end of the third quarter. Effort on consideration of encapsulant materials has been applied earlier than originally planned, to prevent last minute complications in the array encapsulation.

5.2 Future Work

Additional work on cells produced with Ti-doped POCl_3 were done in this quarter with no information contradicting results reported for the first quarter. Results of analyses of Ti concentration in the phosphorus glass layer will be available during the next quarter. More work will be done to assess the role of p+/p back surface field regions on cell performance characteristics in terms of reproducibility and uniformity. Work will continue on metallization development. An assessment of ultrasonic bonding of foil interconnects will be made during the next quarter as well.

Milestones:

1. Approved Development Plan.
2. Preliminary Technical and Economic Evaluation Completed
3. Revised Process Sequence Established.
4. Process Verifications Completed.
5. Proof of Operation Completed.
6. Final Process Plans Established.
7. Material, Supply and Process Specifications and Process Procedures Delivered.

Figure 12
Approximate Task Schedule and Milestone Chart

6. REFERENCES

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