DR. 466

DOE/JPL/954853-2

ARRAY AUTOMATED ASSEMBLY: PHASE 2

Quarterly Report

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May 1978

Work Performed Under Contract No. NAS-7-100-954853

Spectrolab, Inc.
Sylmar, California

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U.S. Department of Energy

Solar Energy

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May 1978

JPL Contract No. 954853

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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.

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ABSTRACT

Surface topography of texturized solar cells was investigated. No significant differences were found between high output and low output cells with a common texturizing treatment. Differences were found between high output and low output cells with a common texturizing treatment. Differences were found associated with variation in the damage removal etch prior to texturizing.

Titania precipitated glasses were found to have suitable properties for use as a diffusion masking dielectric. Preliminary attempts to make solar cells were not successful.

Emulsitone N-250 phosphorous diffusion source was identified to be suitable for solar cell fabrication, and a diffusion procedure was identified.

A number of commercially available fritted silver pastes have been identified as giving promising results. Methods of paste modification by additions of donor source additions and frit content adjustments were found to be effective in proving the performance of some commercial pastes.

Printed silver solder pads on aluminum back contacts were found to be subject to corrosive failure in humidity testing. Tin pads were found to be free of this deficiency.

A module design comprised of an array of 10 by 20 square cells in an area approximately 2 feet by 4 feet was resolved. Projected module efficiency is 12.5%. "LO IRON" sheet glass furnished by ASG Industries was selected for the superstrate as being the most cost effective for projected module costs below \$1.09 per watt.

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1.0 SUMMARY

Surface topography of texturized solar cells was investigated. No significant differences were found between high output and low output cells with a common texturizing treatment. Differences were found associated with variation in the damage removal etch prior to texturizing.

Titania precipitated glasses were found to have suitable properties for use as a diffusion masking dielectric. Preliminary attempts to make solar cells were not successful.

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Printed silver solder pads on aluminum back contacts were found to be subject to corrosive failure in humidity testing. Tin pads were found to be free of this deficiency.

A module design comprised of an array of 10 by 20 square cells in an area approximately 2 feet by 4 feet was resolved on. Projected module efficiency is 12.5%. "LO IRON" sheet glass furnished by ASG Industries was selected for the superstrate as being the most cost effective for projected module costs below \$1.09 per watt.

2.0 INTRODUCTION

This is the second quarterly report for an investigation of technology readiness of a proposed process sequence for the low cost fabrication of photovoltaic modules as a part of Phase 2 of the Array Automated Assembly Task, Low Cost Silicon Solar Array Project. It covers the Quarter ending March 31, 1978.

2.1 TECHNICAL OVERVIEW OF CELL DESIGN AND PROCESS SEQUENCE

The cell design and proposed process sequence are outlined in Table 2-1. Discussion of the module design and process sequence is presented in a subsequent section.

The design included shaped cells in order to achieve the goal of 12-13% module efficiency. During the first quarter an analysis of cost trade-offs showed that the optimum degree of partial shaping from cylindrical crystals would be a circle with small flats, leading to significant unoccupied interstitial areas in the module. We have resolved to use square cells shaped from Czochralski crystals for process verification purposes in anticipation of the eventual availability of square or rectangular sheet material.

Spectrolab's plan includes the use of texturized surfaces, conforming with the conclusions of the Phase 1 studies that this is advantageous. Texturizing is already well developed for (100) oriented single crystal material. During the first quarter it was found that a single step texturizing process is adequate, under some circumstances, to also remove saw damaged surface material.

Table 2-1

CELL DESIGN AND PROCESS SEQUENCE
AS PROPOSED

1. Design:

Shaped, size 25-100 cm² (4-16 in²)

Texturized surface

n+ junction diffusion

p+ back surface field

Printed contact metallization

Wraparound contacts

$\eta_c = 15\%$ (28°C, 100 mW/cm²)

2. Process Sequence:

- 1) Surface Preparation
- 2) Print edge masking dielectric
- 3) Fire edge masking dielectric
- 4) Print back aluminum
- 5) Apply front polymer dopant
- 6) Fire junction and back surface field sources
- 7) Print back isolation dielectric
- 8) Fire back isolation dielectric
- 9) Print contact pads
- 10) Print front grid pattern and wraparound conductors
- 11) Fire contact pads, grid pattern and wraparound conductors
- 12) Test cells

The cell design included a p+ back field obtained from a printed aluminum source. The n+ diffusion was to be obtained from a phosphorus doped polymer source. An innovative approach to the junction formation process was included: namely, the use of a prefired masking dielectric on the edge of the cell. This was intended to permit the codiffusion of the n+ and p+ regions without the need for an edge etch. As a further innovation, it was proposed that the diffusion oxide not be removed, but be retained to serve as an antireflection coating. During the first quarter cofiring of the aluminum back field during diffusion was found to be unsatisfactory. However it was observed that the printed aluminum can be fired through a diffused layer with satisfactory results. This will permit the use of a separate firing step without back etching provided a suitable diffusion mask can be developed.

During the first quarter four glass systems were selected for detailed consideration as edge masking dielectrics. These were beta-spodumene, $\text{MgO-Al}_2\text{O}_3$ borosilicate, baria-magnesia-borosilicate and titania precipitated glasses. During the present (second quarter) it was decided to locate the diffusion mask in a narrow band around the outside perimeter of the back surface rather than on the edge of the cell. The $\text{MgO-Al}_2\text{O}_3$ borosilicate glass series was eliminated and a revised version of the baria-magnesia-borosilicate glass introduced. The titania glass formulation has been tested with positive results as to a diffusion barrier; however, attempts to integrate this process into the total process sequence have not been satisfactory.

A spin-on diffusion source, Emulsitone N-250 has been selected. Sprayon and contact transfer application techniques are being evaluated. During the present quarter it has been determined that retention of the diffusion oxide results in excess series

resistance, and hence its retention as an AR coating is not feasible. However it has been found that under some conditions removal of the diffusion oxide leaves a residual stain which may be suitable for an AR coating.

A further use for the edge masking dielectric was to be as an insulation layer for wraparound contacts. Relocation of the diffusion mask to the back surface eliminates the need for an insulation layer on the cell edge, since the diffused layer will now extend down over the edge. The diffusion mask will continue to serve as an isolation dielectric in its new location.

At this point an additional printing and firing operation was introduced to locate dielectric insulation pads for the wrap-around contacts on the back aluminum. This was followed by printing solderable contacting pads on the back surface. During the present quarter silver contact pads on the aluminum back have been found to be unsuitable because of galvanic corrosion effects. Tin applied by ultrasonic soldering techniques has been found to be more satisfactory. The front metallization grids and wraparound conductors are then printed. For this we proposed using an aluminum thick film paste. Finally, the front contact grids and solderable contacts on the back side would be cofired to complete the cell fabrication. During the first quarter difficulties were encountered with aluminum front contact paste. It was decided to concentrate on developing a screen printed silver paste front contact process. Substantial progress has been made during the second quarter in understanding and improving the performance of screen printed silver front contacts.

The cell design and process sequence as modified by work performed during the first and second quarters is shown in Table 2-2.

Table 2-2

CELL DESIGN AND PROCESS SEQUENCE

Revised April 1, 1978

1. Design:

Shaped, size 5.38 cm square (29 cm^2)

Texturized surface

n+ junction diffusion

p+ back surface field

Printed contact metallization

Wraparound contacts

$\eta_c = 15\%$ (28°C , 100 mW/cm^2)

2. Process Sequence:

- 1) Texture Etch
- 2) Print edge masking dielectric
- 3) Fire edge masking dielectric
- 4) Apply front polymer dopant
- 5) Diffusion
- 6) Print aluminum back
- 6a) Fire aluminum back
- 7) Print back isolation dielectric
- 8) Fire back isolation dielectric
- 9) Print contact pad over dielectric
- 10) Print front grid pattern and wraparound conductors
- 11) Fire contact pad, grid pattern and wraparound conductors
- 11a) Apply tin solder pad on aluminum back
- 12) Test cells

The module design and selected process sequence are shown in Table 2-3. The module design was comprised of a 24 by 48 inch (60 x 120 cm) tempered glass superstrate. Square shaped cells were to be used in order to achieve 12% module efficiency goal. During the present quarter, square cells based on 3 inch diameter Czochralski crystals have been decided on as test vehicles for process verification in anticipation of larger square or rectangular sheet materials becoming available. The crystals will be shaped into prisms with square cross section prior to sawing wafers. The nominal wafer dimension will be 5.38 cm (2.12 inches) on the side. A tentative module design has been prepared comprised of a 10 x 20 cell layout. Cells will be interconnected into a circuit with ten cells in parallel and twenty cells in series. The module is expected to have a peak power of 84 watts at 28°C and 9.4 volts.

The module structure uses a thin bond line adhesive to attach the solar cells to the glass superstrate. Since silicone adhesives were known to be technically feasible, and the thin bond line minimizes costs, they were included in the original design. However, alternative adhesives were to be evaluated in a search for greater cost effectiveness. A large number of adhesive candidates has been evaluated, and a final selection has not yet been made. Silicone adhesives are, however, still leading contenders. Interconnect conductors were to be in the form of thin copper foil mounted on a plastic film. The copper foil would be stamp-cut to preform the interconnects after mounting on the carrier film. A simple automatic reflow soldering operation is permitted by the wraparound techniques used to position both contacts on the back sides of the cells. After

Table 2-3

MODULE DESIGN AND PROCESS SEQUENCE

1. Design

Size 60 x 120 cm (2 x 4 ft)

Tempered glass superstrate

Cells attached by polymeric adhesive

Preformed circuit interconnects

3 mil polymeric conformal coating

Aluminum extrusion frame

$\eta_m = 13\%$

2. Process Sequence*

13. AR Treat Superstrate Glass

14. Mount Cells on Superstrate

15. Cure Adhesive

16. Apply Interconnects

17. Apply Conformal Coat

18. Cure Conformal Coat

19. Mount in Frame

20. Test Module

*Process sequence numbers continue from
the cell area (Table 2-1)

soldering, the carrier film and excess copper foil would be recycled. This scheme has been abandoned because of the costs of recycling the large fraction of material not actually used for interconnects on any one module. Spool fed thin ribbons can be used with equal facility and without generating large amounts of recyclable scrap. The use of flat woven mesh or braid is still under consideration as an alternative material.

A silicone conformal coating was proposed as the encapsulant and rear surface, the module assembly to be completed by mounting the superstrate in an aluminum extrusion frame. A number of coating material candidates have been considered during the first and second contract quarters. Silicone is still a leading candidate, however acrylic and polyurethane candidates have been added for evaluation as possibly being more cost effective. Preliminary designs of the extrusion shapes for the frame have been completed.

3.0 TECHNICAL DISCUSSION

3.1 SURFACE PREPARATION

The texturing of silicon wafers provides an antireflective surface as well as a method of removing damage due to slicing. During this quarter, surface topography was investigated with a Scanning Electron Microscope to distinguish between surfaces generated with the use of a pre-etch to remove surface damage and those produced by direct texture etching of slurry-sawed wafers. Surfaces examined were on cells generated in the previous quarter to study the effect of eliminating the pre-etch⁽¹⁾. Cells were selected for examination to include a high output and a low output cell from three surface treatment groups. The cells, their treatment and electrical parameters are identified in Table 3-1.

All three groups had been etched and/or texturized with solutions of NaOH. A hot, aqueous 30% NaOH solution etches the surface fairly uniformly, but leaves pits about 50 μm in diameter. A hot 2% NaOH, 20% Isopropyl Alcohol, texturing solution has a negligible etch rate in the (111) direction which leaves the (100) surface with four sided pyramids. The rate at which these NaOH solutions attack the surface is dependent on the amount of surface damage, the temperature of the solution, the solution concentration, the relative free-bond density and the solute molecule diffusion through the reaction boundary layer.

The first pair of cells was prepared by slurry-fed ganged slicing followed by cleaning and texture etching with 2% alcoholic NaOH at 80°C for 55 minutes. Figures 1a and 1b show a typical surface region of the higher output solar cell; the surface appears to be free of pitting. The pyramids are broad and have a distribution ranging from 0.2 to

Table 3-1

Cells Examined by SEM for Surface Topography

<u>No.</u>	<u>Pre-Etch Boiling 30% NaOH Minutes</u>	<u>Texture Etch 80°C 2% NaOH* Seconds</u>	<u>E_{oc} Volts</u>	<u>I_{sc} mA</u>	<u>I₅₀₀ mA</u>
1	0.0	55	.612	135	131
2	0.0	55	.604	140	125
3	1.5	55	.612	143	136
4	1.5	55	.602	140	118
5	5.5	55	.613	142	138
6	5.5	55	.599	144	114

*20% by volume Isopropyl Alcohol

to 15 μm with the two extremes disproportionately represented. An average surface section of the lower output solar cell has pits of about 50 μm in diameter, (Figure 2a) and has a slightly higher density of small pyramids (Figure 2b).

The second pair of cells was prepared in a manner similar to Group I but had a 30% NaOH etching treatment at 110°C for 1.5 minutes prior to the texturing treatment. The high output device has pits of 30 to 60 μm (Figure 3a). Small pyramids of about 4 μm in base width diameter and a narrow size distribution appear on the surface (Figure 3b). There seems to be a larger number of deeper pits of the same diameter in the low output solar cell (Figure 4a). The pyramid morphology and density seems to be about the same as that of the high output solar cell (figure 4a).

The third pair of cells had a 5.5 minute 30% NaOH etching treatment prior to texturing. An average surface section of the high output solar cell has very deep 25 μm pits (Figure 5a). The pyramids appear very thin with most of the base diameters being either large ≈ 12 μm or small ≈ 4 μm (Figure 5b). The low output cell does not have many pits (Figure 6a), but does have the same thin shaped pyramids (Figure 6b).

The best solar cells appeared to have minimal pitting with large broad pyramids, height to base diameter ratio of about 0.5 to 1.0. However there does not appear to be a significant difference in the observable surface structure of high and low output cells. Differences in etch treatment lead to differences in observable structure which may be significant in terms of cell output. The overall yield of high output solar cells was degraded as more pre-texturing treatment occurred.⁽¹⁾ The yield progressed: Group 1 > Group 2 > Group 3. The small thin pyramids observed with long pre-etch times may be more susceptible to mechanical damage during the fabrication of the cell, thus resulting in more recombination centers or shunting and poor yield. It must be noted that only one sample of each group was examined microscopically.

Figure 1a. 200X

Figure 1b. 500X

Figure 1. Surface Topography of High Output Solar Cell
Prepared by Texture Etching with No Prior
Damage Removed

Figure 2a. 200X

Figure 2b. 500X

Figure 2. Surface Topography of Low Output Solar Cell Prepared by Texture Etching with No Prior Damage Removed

Figure 3a. 200X

Figure 3b. 500X

Figure 3. Surface Topography of High Output Solar Cell Prepared by Texture Etch After 1.5 Minutes in 30% NaOH Solution at 110°C

Figure 4a. 200X

Figure 4b. 500X

Figure 4. Surface Topography of Low Output Solar Cells Prepared by Texture Etching After 1.5 Minutes in 30% NaOH Solution at 110°C

Figure 5a. 200X

Figure 5b. 500X

Figure 5. Surface Topography of High Output Solar Cell
Prepared by Texture Etching After 5.5 Minutes
in 30% NaOH Solution at 110°C

Figure 6a. 200X

Figure 6b. 500X

Figure 6. Surface Topography of Low Output Solar Cell Prepared by Texture Etching After 5.5 Minutes in 30% NaOH at 110°C

3.2 JUNCTION FORMATION

3.2.1 Diffusion Masking Dielectric

Glass Formation

The glasses for this application were selected on the basis of (1) maturation temperature, (2) resistance to phosphorous diffusion, (3) expansion coefficient, (4) thermal stability, and (5) composition. Specific requirements are as follows:

- 1 - Maturation temperature between 850 and 900°C
- 2 - Thermal expansion coefficient between 3.9 and $4.6 \times 10^{-6}/^{\circ}\text{C}$
- 3 - Capable of being thermal cycled to 850°C and 650°C without loss of adherence to the silicon or dielectric characteristics
- 4 - Oxides comprising the coating shall not reduce the power characteristics of the solar cell.

Based on requirements (1), (2), and (3), five families of glasses were selected as potential candidates. The initial compositions are shown in Table 3-2.

Series 1 - Beta Spodumene Glasses

This family of glass was selected because of low expansion characteristics and low viscosity at about 1090°C. Additionally prescription of spodumene promotes thermal stability.

Series 2 - Magnesia-Alumina Borosilicate Glasses

These glasses are based on a composition from the Ferro Corporation which has a calculated expansion coefficient of $3.9 \times 10^{-6}/^{\circ}\text{C}$, and a maturation temperature of 1010°C.

Table 3-2
Starting Compositions of Diffusion Masking
Dielectrics
Series

Oxide	1	2	3	5	7
<u>Equivalents</u>					
BaO	-	-	0.133	-	0.395
Li ₂ O	0.811	-	-	0.149	-
MgO	0.189	0.875	0.783	-	0.436
CaO	-	0.125	0.043	0.080	0.085
ZnO	-	-	0.041	0.055	0.084
Na ₂ O	-	-	-	0.505	-
K ₂ O	-	-	-	0.211	-
Total	1.000	1.000	1.000	1.000	1.000
B ₂ O ₃	-	1.382	1.753	0.644	0.766
Al ₂ O ₃	0.282	0.330	-	-	-
P ₂ O ₅	0.340	-	-	-	-
	-	-	-	-	-
SiO ₂	3.023	2.334	1.016	2.669	0.857
TiO ₂	-	-	-	1.178	-
<u>Mol Percent</u>					
BaO	-	-	3.52	-	15.06
Li ₂ O	17.46	-	-	2.71	-
MgO	4.07	17.34	20.79	-	16.62
CaO	-	2.48	1.14	1.46	3.24
ZnO	-	-	1.09	1.00	3.20
Na ₂ O	-	-	-	9.20	-
K ₂ O	-	-	-	3.84	-
B ₂ O ₃	-	27.39	46.51	11.73	29.20
Al ₂ O ₃	6.07	6.54	-	-	-
P ₂ O ₅	7.32	-	-	-	-
SiO ₂	65.08	46.25	26.96	48.61	32.67
TiO ₂	-	-	-	21.45	-

Series 3 - Baria-Magnesia Borosilicate

This series has a maturation temperature of 1000°C and a low expansion due to the high content of MgO , B_2O_3 and SiO_2 . This series is similar to Series 7, although the latter has a higher BaO and lower MgO , and B_2O_3 content.

Series 5 - Titania Precipitated Glass

This glass, when smelted and water quenched (i.e., cooled quickly) is transparent. When it is matured on a substrate and cooled slowly (air-quenched) through 620°C and 700°C the titania crystallizes as a mixture of anatase and rutile. This structure is a prime contributor to thermal stability of the coating.

Series 7 - Baria Magnesia Borosilicate

These glasses are similar to those in Series 3; except that initially they contained a higher quantity of BaO and a lower quantity of MgO and SiO_2 . They are therefore "softer" glasses and would tend to have lower maturation temperature than those of Series 3. The Series 7 glasses are lithia and sodium free.

The development of these glasses to meet the requirements stated above are discussed below.

Series 1

The original composition, designated 1E-2, was selected to assure formation of Beta Spodumene, is shown in Table 3-3. This composition did not smelt to a liquid consistency at 1400 to 1500°C . A decrease in silica, increase of P_2O_5 and additions of Na_2O , as shown in composition 1E-8 was required to obtain a smelt which poured readily. The latter composition was applied to silicon and fired for 5 minutes at 800°C . The coating exhibited excellent maturity, but an extremely high wetting angle. The composition was altered by reducing the P_2O_5 content to 1.000 equivalents

Table 3-3

Compositions of 1E Series

Oxide	1E-2	1E-8	1E-11	1E-12	1E-13	1E-14
	<u>Equivalents</u>					
Li ₂ O	0.811	0.649	0.649	0.649 ⁽¹⁾	0.605 ⁽³⁾	0.664 ⁽⁵⁾
MgO	0.189	0.151	0.151	0.151	0.208	0.131
Na ₂ O	-	<u>0.200</u>	<u>0.200</u>	<u>0.200</u> ⁽²⁾	<u>0.187</u> ⁽⁴⁾	<u>0.206</u> ⁽⁶⁾
Total	1.000	1.000	1.000	1.000	1.000	1.000
Al ₂ O ₃	0.282	0.226	0.226	0.226	0.212	0.232
P ₂ O ₅	0.340	1.260	1.000	1.260	1.081	1.287
B ₂ O ₃	-	-	0.250	-	-	-
SiO ₂	3.023	0.850	0.850	0.850	0.796	0.873
SnO ₂	0.050	0.040	0.040	0.040	0.038	0.041

	<u>Mol %</u>					
Li ₂ O	17.27	19.22	19.28	19.22	14.66	19.34
MgO	4.03	4.47	4.49	4.47	5.04	3.81
Na ₂ O	-	5.92	5.94	5.92	4.53	6.00
Al ₂ O ₃	6.01	6.69	6.71	6.69	5.14	6.76
P ₂ O ₅	7.24	37.32	29.71	37.32	26.19	37.48
B ₂ O ₃	-	-	7.43	-	-	-
SiO ₂	64.39	25.18	25.25	25.18	19.29	25.42
SnO ₂	1.06	1.18	1.19	1.18	0.92	1.19

(1) Li₂O Added as 0.701 equivalents LiF

(2) Na₂O Added as 0.217 equivalents NaF

(3) Li₂O Added as 0.675 equivalent LiF

(4) Na₂O Added as 0.209 equivalents NaF

(5) Li₂O Added as 0.710 equivalents LiF

(6) Na₂O Added as 0.220 equivalents NaF

and adding B_2O_3 in the amount of 0.260. This composition, designated as 1E-11, formed a low viscosity melt, but did not mature at a firing temperature of $800^{\circ}C$. The wetting angle did not decrease appreciably. Substitution of LiF for Li_2O and NaF for Na_2O in the 1E-8 (1E-12) reduced the wetting angle. However, the actual maturation and range of maturation temperature was reduced as compared to 1E-8. At $650^{\circ}C$ for five minutes, the coating was underfired, whereas at $740^{\circ}C$ for the same time period, the coating was overfired.

Composition 1E-13, in which the MgO content of 1E-12 increased to 0.120, resulted in a refractory coating system.

It was concluded that the maturation temperature of this coating was difficult to control. In view of the excellent results obtained in processing of the 5E series, this coating system was put into abeyance to be used as a "back-up" system. It should be noted, however, that this system may be a viable candidate for the isolation dielectric systems due to the maturation temperature of 650 to $700^{\circ}C$.

Series 2

The original composition of this series (Table 3-4) did not form a melt at smelting temperatures of $1500^{\circ}C$. Changes in the original composition, e.g., (1) increasing CaF for $CaCO_3$ to obtain CaO in 2E-2, (3) decreasing the MgO content to 0.400 equivalents (2E-3), and (4) further increasing the B_2O_3 content to 5.200 equivalents, did not form a liquid when smelted. The development of this coating system was terminated.

Series 3

These glasses, the compositions of which are shown in Table 3-5, formed high viscosity melts and were too refractory for use as a coating which would mature at $880^{\circ}C$. Modifications of this coating system (Series 7) are discussed below.

Table 3-4
Composition of Series 2E Glasses

Oxide	2E-1	2E-2	2E-3	2E-4
<u>Equivalents</u>				
CaO	0.125	0.125	0.238	0.238
MgO	<u>0.875</u>	<u>0.875</u>	<u>0.762</u>	<u>0.762</u>
Total	1.000	1.000	1.000	1.000
Al ₂ O ₃	0.330	0.330	0.629	0.629
B ₂ O ₃	1.382	2.382	4.537	5.200
SiO ₂	2.334	2.334	4.446	4.446
<u>Mol %</u>				
CaO	2.48	2.07	2.24	2.11
MgO	17.34	14.47	7.18	6.76
Al ₂ O ₃	6.54	5.46	5.93	5.58
B ₂ O ₃	27.39	39.40	42.73	46.12
SiO ₂	46.25	38.60	41.90	39.43

Table 3-5

Composition of 3E Series

Oxide	3E-1	3E-2	3E-3
<u>Equivalents</u>			
BaO	0.133	0.612	0.673
ZnO	0.041	0.190	0.209
CaO	0.043	0.198	0.118
MgO	<u>0.783</u>	<u>-</u>	<u>-</u>
Total	1.000	1.000	1.000
B ₂ O ₃	1.753	8.091	8.882
SiO ₂	1.016	4.691	2.736
<u>Mol %</u>			
BaO	3.52	4.44	5.33
ZnO	1.09	1.38	1.66
CaO	1.14	1.44	0.94
MgO	20.79	-	-
B ₂ O ₃	46.51	58.71	70.39
SiO ₂	26.96	34.03	21.68

Series 5

This coating series, containing dissolved titania as rutile, when smelted and quenched quickly (as when quenched in water) is a clear glass. However, when the glass is reheated and quenched slowly (air quench), through the temperature range of 590 to 650°C, the titania crystallizes primarily as anatase. Upon further reheating, the anatase converts to rutile. These glasses are highly stable when subjected to thermal excursions, and are therefore, based upon thermal characteristics, an excellent system for the masking dielectric.

The original composition (5E-1), as shown in Table 3-6, exhibited a calculated expansion coefficient of $9.94 \times 10^{-6}/^{\circ}\text{C}$. As the expansion was too high for coatings applied to silicon, changes in the composition were made to obtain more compatible expansion values as in 5E-7 and 5E-8. These latter compositions matured to a high gloss, smooth finish at 880°C for 7 minutes.

Coatings 5E-7 and 5E-8 were evaluated as diffusion barriers by subjecting P-type silicon wafers to a diffusion cycle using Emulsitone N-250 phosphorous source. The silicon surface under barrier coated areas was tested by staining techniques and resistivity measurement with no evidence of phosphorous penetration being detected.

Coatings 5E-7 and 5E-8 were further evaluated for their purpose by fabrication of cells after application of the coating. These preliminary experiments yielded cells of poor quality. This result was initially interpreted as being due to contamination of the silicon from the paste during the diffusion step. The titania being suspected as the source of contamination, coating 5E-7-1 was compounded for evaluation. The titania in this coating was replaced entirely by silica. To further identify the contaminant, batches were made in a platinum crucible and a clay crucible. Tests of these materials by

Table 3-6

Series 5 Compositions

Oxide	5E-1	5E-7	5E-8	5E-7-1
<u>Equivalents</u>				
Na ₂ O	0.505	.270 ⁽¹⁾	.219	.270 ⁽¹⁾
K ₂ O	0.211	.088	.093	.088
CaO	0.080	.216	.234	.216
Li ₂ O	0.149	.276 ⁽²⁾	.292	.276 ⁽²⁾
ZnO	<u>0.055</u>	<u>.150</u>	<u>.162</u>	<u>.150</u>
Total	1.000	1.000	1.000	1.000
B ₂ O ₃	0.644	2.752	2.932	2.752
TiO ₂	1.178	1.393	1.489	-
SiO ₂	2.669	7.338	7.823	8.731
<u>Mol %</u>				
Na ₂ O	9.20	2.16	1.65	2.16
K ₂ O	3.84	0.70	0.70	0.70
CaO	1.46	1.73	1.77	1.73
Li ₂ O	2.71	2.21	2.20	2.21
ZnO	1.00	1.20	1.22	1.20
B ₂ O ₃	11.73	22.05	22.14	22.05
TiO ₂	21.45	11.16	11.24	-
SiO ₂	48.61	58.78	59.07	69.94
Expansion Coefficient (x 10 ⁻⁶ /°C)	9.9	5.2	5.2	3.5

(1) Na₂O Added as 0.366 NaF (equivalents)(2) Li₂O Added as .479 LiF (equivalents)

cell fabrication showed no improvement over the original composition, and were possible even inferior.

Another attempt to isolate the contaminant has been initiated. Series 5-E-7-2 through 5-E-7-5 (shown in Table 3-7) are being compounded. The ZnO , Na_2O and Li_2O content was replaced by P_2O_5 (5E-7-2). This composition did not form a melt. Consequently, the silica content has been incrementally reduced in series 5E-7-3 through 5E-7-5. The contamination hypothesis has been subsequently brought into question, and there is a likelihood of confusion from effects due to other process steps.

During this report period, the viscosity characteristics for fusion flow of the Series 5 glasses were determined. The test is conducted as follows:

A one gram sample of -400 mesh powdered glass is formed into a 9.5 mm (3/8 in.) diameter pellet at a minimum pressure of 28500 psi (1000 lbs load). The pellet is placed on a silicon wafer and fired at 980°C (100°C above the maturation temperature), in a horizontal position for 1.5 minutes. Without removing from the furnace, the wafer is tilted 90° and the pellet is fired for 7.0 minutes in the vertical position. The flow of the melted glass is measured to the nearest 0.5 mm.

The fusion flow characteristics of the 5E-7, 5E-8, 5E-7-1 and 5E-7-1-P samples are shown in Table 3-8. It can be noted that Series 5E-7 has a longer fusion flow than 5E-8, due to the higher Na_2O content. A major point of interest is the higher fusion flow of 5E-7-1-P as compared to 5E-7-1. Both series are the same composition, except that 5E-7-1 was smelted in a clay crucible, whereas 5E-7-1-P was smelted in a platinum crucible. The observed difference indicates solubility of the clay crucible in the melt. Additionally, the results of substituting silica for titania (5E-7 and 5E-7-1) can be noted.

Table 3-7

Series 5E Compositions
with Added P_2O_5

Oxide	5E-72	5E-73	5E-74	5E-75
<u>Equivalents</u>				
K_2O	0.288	0.288	0.288	0.288
CaO	<u>0.712</u>	<u>0.712</u>	<u>0.712</u>	<u>0.712</u>
Total	1.000	1.000	1.000	1.000
B_2O_3	9.041	9.041	9.041	9.041
SiO_2	38.676	20.000	15.000	10.000
P_2O_5	3.505	3.505	3.505	3.505
<u>Mol %</u>				
K_2O	0.55	0.86	1.01	1.22
CaO	1.36	2.12	2.49	3.02
B_2O_3	17.31	26.95	31.67	38.40
SiO_2	74.06	59.62	52.55	42.47
P_2O_5	6.71	10.45	12.28	14.89
Expansion Coefficient ($\times 10^{-6}/^{\circ}C$)	3.3	3.4	3.5	3.7

Table 3-8

Flow of Series 5
at 980°C and 7 Minutes

Test	Series Number	Flow (mm)	Remarks
1	5E-7	29.5	
2	5E-8	23.5	Lower Na ₂ O content than 5E-7
3	5E-7-1	24.3	*Smelted in clay crucible
4	5E-7-1-P	39.3	*Smelted in platinum crucible
No titania in 5E-7-1 and 5E-7-1-P			

*Compositions are the same

This testing will be valuable in assessing the effect of changes in composition upon maturing temperature. This application of the test will be illustrated in the discussion of the Series 7 glasses.

Coatings 5E-7 and 5E-8 were evaluated for thermal endurance. The coatings were cycled ten times from room temperature to 880°C and back to room temperature (Series A). The color of the coatings changed from a blue white to a yellow white indicating that the crystallized titania was converted from anatase to rutile. cursory examination of the exposed silicon adjacent to the coating indicated a blue haze which became more pronounced as the thermal cycling progressed. The coatings were also sequentially cycled from room temperature to 880, 800 700 and 600 and 500°C (Series B).

Coated silicon wafers, representative of both thermal cycling sequences, were examined with the Scanning Electron Microscope. The area adjacent to the coatings were examined with the microprobe.

Series 7

The study of this series was initiated as a back-up to Series 5. These coatings, as shown in Table 3-9, are free of Na₂O and Li₂O. The initial compositions (7E-1 and 7E-3) evaluated for degree of maturation at a firing temperature of 880°C for 7 minutes indicated an overfired condition. Additionally, the expansion coefficient (calculated) was too high for application to silicon. The magnesia content was increased in 7E-3 to obtain a reduced coefficient of expansion and at the same time increase the maturation temperature. From examination of Table 3-9 the reduction in expansion coefficient can be noted.

Table 3-9. Series 7 Compositions

Oxide	7E-1	7E-3	7E-4	7E-5	7E-6	7E-7	7E-8	7E-9
	<u>Equivalents</u>							
BaO	0.412	0.395	0.395	0.359	0.329	0.304	0.198	0.260
ZnO	0.088	0.084	0.084	0.076	0.070	0.065	0.042	0.055
CaO	0.089	0.085	0.085	0.077	0.071	0.065	0.042	0.056
MgO	<u>0.412</u>	<u>0.436</u>	<u>0.436</u>	<u>0.487</u>	<u>0.530</u>	<u>0.566</u>	<u>0.718</u>	<u>0.629</u>
Total	1.001	1.000	1.000	0.999	1.000	1.000	1.000	1.000
Al ₂ O ₃	0.014	-	-	-	-	-	-	-
B ₂ O ₃	0.634	0.766	0.766	0.696	0.638	0.489	0.386	0.506
SiO ₂	0.895	0.857	0.657	0.597	0.548	0.505	0.329	0.433
ZnO ₂	0.029	-	-	-	-	-	-	-
	<u>Mol %</u>							
BaO	16.01	15.06	16.30	15.66	15.05	14.52	11.52	13.41
ZnO	3.42	3.20	3.47	3.32	3.20	3.10	2.45	2.85
CaO	3.46	3.24	3.51	3.36	3.25	3.10	2.48	2.89
MgO	16.01	16.62	17.99	21.25	24.25	27.03	41.88	32.43
Al ₂ O ₃	0.54	-	-	-	-	-	-	-
B ₂ O ₃	24.64	29.20	31.61	30.37	29.19	28.13	22.51	26.09
SiO ₂	34.78	32.67	27.12	26.45	25.07	24.12	19.16	22.32
ZnO ₂	1.13	-	-	-	-	-	-	-
Expansion Coefficient (x 10 ⁻⁶ /°C)	5.2	4.9	5.0	4.6	4.5	4.4	3.9	4.3

Based on the work on Series 5 discussed above, it was decided that the Series 7 glasses, should exhibit a fusion flow length between 20 and 30 millimeters at an exposure of 980°C , with $1\frac{1}{2}$ minutes in the horizontal position and 7 minutes vertically. Based on the data shown in Table 3-10 all of the glasses, with the exception of 7E-8, would be overfired at a temperature of 880°C . Coating 7E-8 would be underfired. As the magnesia content was increased above that shown in 7E-5, adherence decreased drastically. The adherence was restored upon the addition of 5 parts of Lepo Fluoride (PbF_2) to 100 parts by weight of glass.

Mixtures of glasses 7E-6, 7E-7 and 7E-8 were made to determine the optimum magnesia and lead fluoride content to obtain good adherence and maturation at 880°C (Table 3-11). Adherence was noted only at lead fluoride contents of 5 parts per 100 parts by weight of glass. The composition of 7E-8-1 was determined on the basis of tests 4, 5 and 10 through 17. An anomaly exists in tests 19 through 21. It would be expected that an increasing lead fluoride content should increase the fusion flow. However, since lead fluoride contents less than 5.0 did not result in adherence, the reasons for the anomaly may be academic. Coating 7E-8-1 will be prepared for evaluation as a diffusion barrier.

Table 3-10

Flow of Series 7
at Various Times and Temperatures

Test	Series Number	Time* (min)	Temp (°C)	Flow (mm)	Remarks
1	7E-2	980	4	>46.0	
2	7E-3	980	3	27.0	
3	7E-4	980	2	>46.0	
4	7E-7	980	7	>51.0	
5	7E-8	980	7	13.5	(devitrified)
6	7E-5	900	4	40.8	
7	7E-6	900	4	36.8	
8	7E-7	900	4	32.3	
9	7E-8	900	4	17.8	

Table 3-11

Flow of Series 7* @ 980°C, 7 Min.

Test No.	7E-6	7E-7	7E-8	7E-8-1	PbF ₂	Flow (mm)
4	-	100	-	-	0	51.0
5	-	-	100	-	0	13.5 (Devitrified)
10	-	50	50	-	0	19.0
11	-	70	30	-	0	34.0
12	-	70	30	-	2.5	47.5
13	-	70	30	-	5.0	48.5
14	-	-	100	-	5.0	0
15	40	-	60	-	5.0	18.0
16	45	-	55	-	5.0	20.5
17	50	-	50	-	5.0	48.5
18	-	-	-	100	0.0	46.8
19	-	-	-	100	5.0	22.0
20	-	-	-	100	4.5	33.5
21	-	-	-	100	4.0	24.5

*Parts by Weight

3.2.2 P⁺ Back Contact

A number of cell fabrication experiments have been carried out in order to understand the effectiveness of an Al back contact metallization both as ohmic contact and its ability to remove the diffused N⁺ layer. These experiments are summarized in Table 3-12. In all cases cells were fabricated on 2 inch diameter 10 ohm cm P-type round wafers. Surfaces were prepared by a damage removal etch in hot 30% hydroxide with no texturizing. Junctions were formed at a depth of 0.3 μ m by phosphine diffusion. Front contacts were evaporated Ti-Pd-Ag after removal of the diffusion oxide by 10 second immersion in 5% HF. Back contact preparation was varied as indicated in Table 3-12. No AR coat was applied. After cell processing was completed, 2 x 2 cm cells were cut from the round disks in order to provide edge clean up.

The first experiment demonstrates the problem of producing a cell without removing the diffused N⁺ layer. Once the N⁺ layer is removed by back etching (experiment 2), the back contact is able to make ohmic contact. In this experiment, the cells have a relatively low V_{oc} and I_{sc} characteristic of 10 ohm-cm material without a back field. On firing an Al back contact to produce a P⁺ layer (experiment 3), the V_{oc} increased 10% and the I_{sc} increased 5%. The ability of the P⁺ layer to remove the N⁺ layer during firing is shown in experiment 4. Comparison of this experiment with the preceding one suggests that the back etch process used in experiment 3 somehow contributes to degradation of cell, possibly by damage to the front surface. Experiment 5 in which the aluminum back was fired at a lower temperature indicates the sensitivity of the process to the firing cycle.

Table 3-12
Formation of P⁺ Back Contact Through
Diffused Layers

Exp.	Back Etch	Back Contact	Firing Condition	E _{oc} mV	I _{sc} mA	I ₄₀₀ mA
1.	no	Evap.	none	no response		
2.	yes	Evap.	none	542	89	88
				538	88	87
				538	86	85
				538	85	84
				541	89	88
				541	90	89
				536	86	85
				541	89	88
				539	87	86
				538	88	87
			$\bar{X}$	539	87.7	86.7
			σ	1.87	1.55	1.55
3.	yes	Paste Al	10 sec. 900°C	600	94	83
				597	96	96
				596	98	96
				589	95	92
				585	94	93
				588	95	93
				571	94	90
				563	92	89
				592	96	95
				580	93	91
			$\bar{X}$	586	94.7	91.8
			σ	11.2	1.61	3.71
4.	no	Paste Al	10 sec 900°C	604	97	95
				604	96	95
				601	96	95
				600	97	96
				603	95	95
				596	96	95
				605	96	95
				602	97	96
				601	96	95
				605	95	94
				602	97	96
				600	96	96
				604	96	95
				604	96	95
			$\bar{X}$	602	96.1	95.2
			σ	2.40	0.63	0.558

Table 3-12 (continued)
Formation of P⁺ Back Contact Through
Diffused Layers

Exp.	Back Etch	Back Contact	Firing Condition	E _{oc} mV	I _{sc} mA	I ₄₀₀ mA
5.	no	Paste Al	15 sec 800°C	589	95	92
				584	94	93
				588	95	93
				571	94	90
				563	92	89
				592	96	95
				563	92	86
				580	93	91
				$\bar{X}$ 579	93.9	91.1
				σ 10.9	1.36	2.61

3.2.3 Diffusion

During the present quarter diffusion process work has concentrated on the use of Emulsitone N-250 diffusion source. This source material was successfully applied by spraying and contact transfer techniques to yield uniform junctions and efficient solar cells. It was found that if the applied layer is too thick, it may flake during drying. This observation probably accounts for the unsatisfactory performance previously observed with this source.⁽²⁾ This thickness limitation was less stringent for texturized than polished or semi-polished cells. Better control of the sprayed layer thickness was achieved through dilution of the N-250 by the addition of anhydrous isopropyl alcohol to 30% volume concentration. The applied diffusion source was fired in a nitrogen atmosphere with a 25 minute ramp from 700°C up to 900°C, a ten minute drive at this temperature and a 25 minute ramp back down to 700°C in all cases.

This diffusion cycle for N-250 was tested on four sets of cells with variations in surface preparation and method or dopant application. In all cases the cells were fabricated on 10 ohm cm silicon wafers with evaporated contacts and P+ back surface field 2 cm x 2 cm cells were cut from rounds after completion of all processing. Results are reported in Table 2-13, together with the surface, treatment and method of application.

Table 3-13

Output parameters at AMO for non-AR coated cells prepared by diffusion from N-250 source with a diffusion cycle of 25 minutes ramp from 700°C to 900°C, 10 minutes at 900°C, 25 minute ramp from 900°C to 700°C.

Experiment	Treatment	V _{oc}	I _{sc}	I ₄₀₀
1.	Surface texturized to a matte finish. Undiluted N-250 applied by spraying. Some diffusion residue was resistant to HF, and acted as an AR coating.	620	141	140
		616	140	138
		617	137	135
		619	141	139
		614	141	137
		619	137	135
		616	139	138
		616	139	137
		$\bar{X}$	517.1	139.4
		σ	1.90	1.58
2.	Surface texturized to form sharply defined pyramids. Undiluted N-250 applied by spraying. Diffusion glass removed by HF soak (30 sec. in 5% HF)	613	137	134
		613	132	129
		612	129	128
		614	129	128
		612	138	128
		613	139	130
		614	134	130
		616	135	130
		615	134	132
		$\bar{X}$	613.6	134.1
		σ	1.26	3.41
3.	Surface texturized to a matte finish. N-250 applied by contact transfer from Dextilose paper. Diffusion glass removed by HF soak (30 sec in 5% HF)	616	128	126
		612	129	121
		613	127	124
		614	134	126
		614	128	124
		618	137	134
		612	132	131
		612	132	131
		616	130	128
		618	130	129
		618	129	127
		616	129	127
		$\bar{X}$	614.9	130.4
		σ	2.29	2.75
				3.42

Table 3-13 (continued)

Experiment	Treatment	V _{oc}	I _{sc}	I ₄₀₀
4.	Surface smooth etched in 30%	613	107	106
	NaOH. N-250 applied by contact	610	112	108
	transfer from Dextilose paper.	604	108	91
	Diffusion glass removed by HF	606	106	94
	soak (10 sec in 5% HF)	609	113	99
		610	110	87
		612	106	93
		613	108	92
		602	107	93
		$\bar{X}$ 608.4	108.6	95.9
		σ 3.77	2.40	6.64

The first group of samples were sprayed with a heavy layer of undiluted N-250. Care was necessary in order to prevent flaking upon drying; polished samples had a higher tendency for flaking. A stain layer remained on the surface after a 5% HF etch following diffusion. These cells tested very good P^+ . The group 2 cells were sprayed with N-250 that had been diluted with 30% IPA. Very thin layers of N-250 were applied and no stain layer remained after the 5% HF etch. These cells also provided very good response, however, I_{sc} is lower than group 1, suggesting that the stain in that group acted as an antireflective coating. N-250 was applied to the third group by means of a contact transfer and produced good cells. Contact transfer of N-250 onto nontextured cells (group 4) also produced good cells with a reduced output resulting from lack of texturing.

Additional experiments were carried out on 2 ohm-cm wafers. In these the diluted N-250 source was sprayed on and diffused at a lower temperature (850°C for 30 minutes). In one experiment an aluminum back was applied, in the other an evaporated back etching. The results are reported in Table 3-14. In both cases good cells were obtained with output at load comparable to cells in the previous experiments. In this experiment the aluminum back did not cause the expected increase in open circuit voltage and short circuit current.

Table 3-14

Output parameters at AMO for non-AR coated cells prepared by diffusion from N-250 source with a diffusion cycle of 20 minutes ramp from 700°C to 850°C, 30 minutes at 850°C, 20 minute ramp from 900°C to 700°C.

Experiment	Treatment	V _{oc}	I _{sc}	I ₄₀₀
1.	Texturized surface. Diluted N-250 applied by spraying. Diffusion glass removed by soak in HF (10 sec in 5% HF) Aluminum back contact.	599	133	129
		597	136	129
		602	139	133
		600	130	120
		600	134	128
		$\bar{X}$ 599.6	134.4	127.8
		σ 1.62	3.01	4.26
2.	Texturized surface. Diluted N-250 applied by spraying. Diffusion glass removed by soak in HF (10 sec in 5% HF) Evaporated back contact.	600	144	143
		604	147	138
		599	147	132
		599	146	135
		602	146	134
		549	147	131
		603	145	133
		598	147	125
		601	147	136
		600	145	131
		599	145	132
		603	146	134
		600	146	132
		601	146	129
		603	145	135
		598	146	133
		$\bar{X}$ 600.5	145.9	133.4
		σ 1.85	0.90	3.8

3.3 METALLIZATION

3.3.1 Front Contacts

During the current period, work was continued on the use of fritted thick film pastes as contact metallization. The commercial silver pastes listed in Table 3-15 have been evaluated with respect to output of cells fabricated with various firing cycles.⁽¹⁾ Those pastes indicated by asterisks are those giving better results as received from the vendor.

Guided by the hypothesis of oxidative attack of the silicon accomplished by solution of the SiO_2 in the frit during the firing process, we have investigated the effects of varying the amount of frit in the paste and additions of N type diffusion sources. In general both of these lead to improved performance.

The optimum frit content is usually less than that normally present in commercial pastes and appears to be about 2%. The effect of reducing the frit content of Cermalloy 4450 silver paste by the addition of Thick Film Systems A-250 fritless silver paste is shown in Figure 7.

Emulsitone 233(Sb) and Transene N-Diffusol have been found to be useful additives in the amounts of about 2% by weight. The effect of adding Emulsitone 233(Sb) to Electro-Science Laboratories 590 silver paste is shown in Figure 8. These diffusion source additives frequently have the effect of reducing the sensitivity of the time-temperature firing cycle.

3.3.2 Solder Pads

One disadvantage of an aluminum back contact is the anodic nature of aluminum. The galvanic series for aluminum and some

Table 3-15
COMMERCIAL AG PASTES
EVALUATED FOR USE AS COLLECTOR METALLIZATION

AVX	6080
Cermaloy	4450
DuPont	7095*
.	7713
.	8032
Electromaterials	AG-6058-1
.	AG-92*
Electroscience Lab	590*
Englehard	E-439-A/B*/C
.	A2735
.	A2921 (Mod. 025)*
.	A3233
Methode Dev. Co.	3521
.	3522
Plessey	L15-1260-T1
Thick Film Systems	A250 (Fritless)
.	A256*
.	A268
.	A3330
Transene	100
.	200

*Pastes giving better results as received from vendor.

Figure 3-17

IMPROVEMENT OF CURVE SHAPE
BY REDUCING FRIT CONTENT OF PASTE

Figure 18

EFFECT OF N-TYPE DIFFUSION SOURCE
ADDITION TO COMMERCIAL SILVER PASTE ON
SOLAR CELL PERFORMANCE

other important metals is:

ANODE

zinc

aluminum

lead-tin solders

copper

nickel

silver

CATHODE (least corrodable)

The use of a silver solder pad on top of the aluminum for soldering may lead to corrosion and delamination of the silver.

A fritted and a frit-free silver paste were printed on top of the aluminum metallization. Samples were exposed to 100% humidity at 65°C for 7 days. Both materials peeled to some degree, with the frit-free material showing poorer adherence. Zinc and indium additives to the aluminum were tested. This modification did not improve the corrosion resistance of the aluminum-silver couple in humidity testing. The use of a precious metal paste (TRS 3402 Pd-Ag) offered no adherence advantage over less expensive materials such as DuPont 7095. The use of a high frit paste such as TFS 3303 (~ 15% frit) resulted in improved humidity tolerance with an unfortunate concurrent loss in solderability.

Tin and 90% tin-10% zinc solder pads were applied to the aluminum back contact metallization by ultrasonic soldering techniques. Interconnects of tin and lead-tin plated copper mesh were soldered to cells with these solder pads. These interconnects were pre-pulled at 90° to approximately 1000 grams, Table 3-16. The cells with interconnect that did not fail during the pre-pull

test were subjected to 100% humidity at 70°C for 168 hours. The cell interconnects were then re-pulled to failure (Table 3-16). These combinations demonstrated good adherence and tolerance to humidity. The tin-zinc pads experienced a small degree of corrosion whereas the tin did not change during the exposure.

Table 3-16

BACK CONTACT METALLIZATION
SOLDER TO ALUMINUM P⁺
by Ultrasonic Soldering Pad

Cell No.	Pad	Solder	Flux	Pre-Pull Test (grams)	Pull Test After Humid. (grams)
1	Sn	Pb-Sn	α -611	1550	1375
23	"	"	"	1050 *	-
24	"	"	"	1060	1600
25	"	"	"	1110	1275
26	"	"	"	1060	1200
3	Sn	Sn	organic	1150 *	-
4	"	"	"	750 *	-
5	"	"	"	850 *	-
17	"	"	"	980	1100
18	"	"	"	1130	1250
19	"	"	"	960	1180
20	"	"	"	1030	425
6	Sn-.1Zn	Pb-Sn	α -611	1040	1025
32	"	"	"	1110	675
33	"	"	"	1030	775
34	"	"	"	1100	775
35	"	"	"	960	700
36	"	"	"	1050	800
37	"	"	"	1140	700
8	SN-.1Zn	Pb-Sn	organic	800	-
9	"	"	"	1220	1100
10	"	"	"	1000	-
27	"	"	"	1040	1200
28	"	"	"	925	800
29	"	"	"	960	1050

*failure by cell breakage.

3.4 Module Assembly

3.4.1 Bonding and Back Coating Materials

The current status of candidate materials which have been considered for cell to superstrate bonding and for module back coating is reviewed in Tables 3-17 and 3-18 respectively.

Testing of candidate adhesive materials was continued and Table 3-19 reviews the bond strength-environmental exposure tests made to date. The greatly reduced strength of glass to glass relative to cell to cell bonds with the RTV-615/4120 primer system after humidity exposure appears to be anomalous and will be further investigated.

Table 3-17

Status of Candidate Adhesive Materials

Manufacturer	Identification	Type	Comments
<u>Retained for further consideration</u>			
General Electric	RTV 615	Silicon RTV	
Loctite	353	Acrylic UV cure	
Loctite	524	Acrylic heat cure	
Shell	Epon 828/Versamid 125	Epoxy	
Dow Corning	X3-6558	Siliconegel	Poor adhesion and permanently soft, tacky surface
<u>Eliminated</u>			
Dow Corning	Q1-2577 (mica)	Silicone B stage	Poor light transmission
Dennison	Densil tape	Double Backed	Bubbles and unbonded areas
Loctite	Loctite 524/525	Acrylic/accelerator	Poor light transmission
Hughson	Versilock 506/4	Acrylic/accelerator	Poor light transmission
Hughson	Versilock 521/4	Acrylic/accelerator	Poor light transmission
Franklin	Rexite P2/SB	Acrylic/accelerator	Poor light transmission
Hysol	EA9446 A/B	Acrylic/accelerator	Poor light transmission
Ciba-Geigy	DA-56C-4	Acrylic UV Cure	Poor temperature resistance
Rohm and Haas	Acryloid B-7	Acrylic, Thermo-plastic	Bubbles and unbonded areas, poor temperature resistance

Table 3-18

Status of Candidate Protective Coating Materials

Manufacturer	Identification	Type	Comments
		Retained for Further Consideration	
Dow Corning	Q1-2577	Silicone Coating	
Dow Corning	R-4-3117	Silicone Coating	
Dow Corning	X3-5035	Silicone Emulsion	
Contour Chem. Co.	XB-1786	Silicone Coating	
Product Techniques	PT 469 Clear	Modified Acrylic	
Photo Chem Prod.	Perma Resin	Epoxy-Acrylic	
Bostic Finch	MIL-C-83286	Polyurethane	
Deft Chem. Coat.	MIL-L-81352	Acrylic	
Rustoleum	C-1590 white	Alkyd	

Eliminated

General Electric	RTV 615	Silicone	Poor adhesion
Rohm & Haas	QR-568/	Oxazolidine Acrylic/	Delamination during
Mobay	Desmodure N75	Polyurethane	thermal cycle
Dow Corning	Q3-6553	Silicone Gel	Low strength permanently
			tacky surface
Rohm & Haas	Acryloid B-7	Acrylic	Poor adhesion

Table 3-19

BOND STRENGTH/EXPOSURE
LAP SHEAR STRENGTHS LBS/IN²
(AVERAGE APPROX. 10 SPECIMENS)

<u>MATERIAL</u>	AS BONDED		AFTER THERMAL CYCLE -40° to 100°C		AFTER HUMIDITY 95% @ 70°C	
	<u>CELL</u>	<u>GLASS</u>	<u>CELL</u>	<u>GLASS</u>	<u>CELL</u>	<u>GLASS</u>
RTV615	145	173	86	191	250	218
RTV615/4120 Prim	330	250	195	238	310	95
RTV615/4155 Prim		205		234		266
X3-6558	7.5	123	8.5	125	12.3	161
Loctite 524	812	448	566	428	368	280
Epon 828/Vers 125	744	284	272	273	436	278
Loctite 353 U.V.	527	572	102	591	468	453

3.4.2 Glass Evaluation

A 16 cell laminated module has been adapted for evaluation of light transmission properties. The material to be tested is placed on the glass face plate of the laminated module. Cyclohexane (index of refraction = 1.42662) is used as an optical coupling agent to minimize reflections at the interface between the test material and the glass module face. The current-voltage curve is measured in a solar simulator with and without the test specimen in position. The combined effect of test material absorption and difference in the reflection between the test material and glass module surface can be inferred from the observed short circuit current.

Samples of double strength (0.125 inch) low iron content sheet glass (LO-IRON) and water clear (SUNADEx) glass obtained from ASG Industries Inc. were tested in this equipment. These glasses are specified by the manufacturer to have nominal iron contents of 0.05% and 0.01% respectively. Observed values of short circuit current and current at a test voltage of 7.2 volts are reported in Table 3-20. Since in this case the test samples are glass, the difference in reflection will be zero to a first approximation. The observed effects are therefore all attributable to absorption. Although not measured in this experiment, we have observed that ordinary float glass (iron content 0.12%) causes a reduction in output of the test module of 6 to 12 percent.

Table 3-19

Transmission Measurements of 1/8" thick SUNADEX glass and LO-IRON sheet glass using 16 cell solar circuit test panels.

Sample	I_{sc} (mA)	$I_{7.2}$ (mA)	V_{oc} (V)	% Change		
				I_{sc} (mA)	$I_{7.2}$ (mA)	V_{oc} (V)
Test Panel	649	580	9.32	-	-	-
LO IRON	627	565	9.31	-3.39	- 2.58	-0.11
SUNADEX	642	577	9.30	-1.08	-0.52	-0.21

We have received quotes for large quantities of SUNADEX and LO-IRON and float glass from ASG Industries which are given in Table 3-19. Using this cost data and the transmission data from Table 3-18 one can estimate the relative cost effectiveness of these two glasses. Assuming a module efficiency of 12% with the use of LO-IRON glass, the 2% increase in output (at load) with SUNADEX glass would result in module power increasing from 11.15 watts per square foot to 11.37 watts per square foot. The increase of 0.22 watts would cost \$1.09 per watt $(\$0.69 - 0.45) \div 0.22$. Thus under the assumed conditions, use of SUNADEX glass would be cost effective only if the base line module cost exceeds \$1.09 per watt.

3.4.3 Module Design

The proposed module design and selected process sequence are shown in Table 2-3. The module design was comprised of a 24 by 48 inch (60 x 120 cm) tempered glass superstrate. Square shaped cells were to be used in order to achieve 12% module efficiency goal. During the present quarter, square cells cut from 3 inch diameter Czochralski crystals have been decided on

Table 3-21

Glass prices for large quantity purchases of standard sizes furnished in standard cases. Minimum of 20 cases of one type of glass. Source: ASG Industries, Kingsport, Tennessee.

Thickness inch	Std. Size inch	Price \$ per sq. ft.		
		SUNADEX	LO IRON sheet	STARLUX float
1/8	34 x 76	.69	.45	.47
5/32	34 x 76	.80	.53	NA
	34 x 84	NA	.53	NA
	34 x 96	.80	NA	NA
3/16	34 x 76	NA	.61	.51
	34 x 96	.91	NA	NA
	46 x 76	.91	.61	.51
	46 x 84	NA	.61	.51
	46 x 92	NA	NA	.51
	46 x 96	.91	NA	NA
7/16	46 x 96	1.03	NA	NA

Standard Case Weight & Footage

	SUNADEX	LOW IRON	STARLUX
*1/8	2000# 1200'	2000# 1200'	3000# 1200'
5/32	2000# 1000'	2000# 1000'	NA
3/16	2000# 900'	2000# 900'	2700# 1000'
7/16	2000# 700'	NA	NA

*Shipping cost .12 per sq. ft.

as test vehicles for process verification in anticipation of larger square or rectangular sheet materials becoming available. The crystals will be shaped into prisms with square cross section prior to sawing wafers. The nominal wafer dimension will be 5.38 cm (2.12 inches) on the side. A tentative module design (Figure 9) has been prepared comprised of a 10 x 20 cell layout. Cells will be interconnected into a circuit with ten cells in parallel and twenty cells in series. Figure 10 shows the superstrate design for this circuit. This design could be easily modified into a circuit with five cells in parallel and forty cells in series. These circuits are expected to have a peak power of 84 watts at 28°C and either 9.4 or 18.8 volts respectively. This is based on an assumed 15% cell efficiency. The corresponding module efficiency is

$$\frac{2.12^2 \times 200 \text{ (cell area)}}{16.03 \times 23.35 \text{ (module area)}} \times 15\% = 12.5\%.$$

4.0 CONCLUSIONS

The following conclusions have been drawn on the basis of the work reported here:

- a. Differences in cell output are not relatable to observed differences in the surface topography of individual cells within cell lots subjected to a given texture etch surface treatment.
- b. Prolonged pre-etch to remove surface damage induces the formation of thin pyramids during the texture etch which may be associated with a higher incidence of low output cells as a consequence of greater pyramid fragility.
- c. Magnesia-alumina-borosilicate glass are not satisfactory for consideration as diffusion masking dielectrics because of excessive refractoryness.
- d. Titania precipitated glass has properties, (refractoryness, contact angle, expansion coefficient, adhesion and maturation temperature) suitable for processing as a diffusion dielectric and has diffusion barrier behaviour in preliminary tests with Emulsitone W-250 phosphorous diffusion source. However, problems have been encountered in incorporating the process into the cell processing sequence.
- e. Emulsitone W-250 is a suitable phosphorous diffusion source for the fabrication of solar cells.
- f. Several commercial fritted silver screen printing pastes are suitable candidates for front contact metallization. Commercial pastes can sometimes be improved by adjusting the frit content and/or by adding donor sources.
- g. Printed silver solder pads are unsuitable on aluminum back contacts due to their susceptibility to corrosive attack by water vapor.

- h. Tin solder pads on aluminum back contacts are resistant to corrosive attack.
- i. Low iron sheet glass is more cost effective than water clear (SUNADEx) glass for use as a module superstrate if module cost is less than \$1.09 per watt according to current large volume price quotations.

5.0 RECOMMENDATIONS

There are no recommendations.

6.0 NEW TECHNOLOGY

There was no new technology reported during the quarter.

7.0 REFERENCES

1. W.E. Taylor, Array Automated Assembly, Phase 2, (Sylmar, California: Spectrolab, Inc.) JPL Contract 954853, Quarterly Report (February, 1978), DOE/JPL954853-78/1
2. J.W. Thornhill, Automated Fabrication of Back Surface Field Silicon Solar Cells with Screen Printed Wraparound Contacts, (Sylmar, California, Spectrolab, Inc.), NASA/LRC Contract NAS3-20029, Final Report, (August, 1977), NASA CR-135202.