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ARRAY AUTOMATED ASSEMBLY. PHASE 2

Quarterly Report, June 30, 1978

By
William E. Taylor
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Angel Pepe

August 1978

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

Spectrolab, Incorporated
Sylmar, California

MASTER

U.S. Department of Energy

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PHASE 2

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For the Quarter ending June 30, 1978

Prepared by:
William E. Taylor, William Kimberly
Nick Mardesich, and Angel Pepe

August 1978

JPL Contract No. 954853

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MASTER

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 by NASA and DOE.

ABSTRACT

The Automated Array Assembly Task, Phase 2 of the Low Cost Solar Array Project is a process development task. The overall goal is to advance solar cell and module process technology to meet the 1986 goal of a production capacity of 500 megawatts per year at a cost of less than \$500 per kilowatt. Work performed during the Quarter ending June 30, 1978 is covered in this report.

The report includes discussions of diffusion masking dielectric evaluation, P+ back surface fields formed by firing screen printed aluminum back contacts, screen printable glass systems for use as isolation dielectrics, screen printed front contact metallization and stresses caused by thermal cycling silicon solar cells adhesively bonded to glass superstrates. SEM pictures of the fritted layer at the interface between the front metallization and silicon are presented. Results of an x-ray topographic examination of the silicon under and adjacent to printed and fired patterns of fritted conductor and dielectric pastes are given.

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1.0 SUMMARY STATEMENT

Evaluation of screen printed diffusion masking dielectrics has been confused by low shunt resistance arising from unidentified sources. However, it has been possible to continue the investigation and development of front and back metallization processes. Aluminum screen printing pastes have higher optimal firing temperatures than those previously reported for fritted silver front metallization. The firing time must be short, on the order of one minute or less. Optimum firing time and temperature depend on the specific paste formulation.

A number of screen printable dielectrics have been investigated and are being refined for evaluation for use as isolation dielectric. Problems have been encountered with bubble formation, maturation temperature and expansion coefficients.

Scanning electron microscope evaluation of the fritted layer at the interface between the front metallization and silicon did not reveal any significant difference between pastes which produce cells of different performance. X-ray fluorescence analysis suggested that the presence of aluminum in the front metallization paste is detrimental. This was confirmed by the fabrication of cells using pastes prepared with aluminum free frits.

X-ray topographic examination of silicon under and adjacent to printed patterns of fritted conductor and dielectric pastes revealed no evidence of structural damage. The samples had been thermal cycled to simulate the cell fabrication process sequence.

2.0 INTRODUCTION

This is the third quarterly report of an investigation of technology readiness of a proposed process sequence for the low cost fabrication of photovoltaic modules as part of Phase 2 of the Array Automated Assembly Task, Low Cost Silicon Solar Array Project. It covers the Quarter ending June 30, 1978.

2.1 TECHNICAL OVERVIEW OF CELL DESIGN AND PROCESS SEQUENCE

The cell design and process sequence as modified by work performed to date are shown in Table 2-1. Steps where major modifications have been made in the process sequence are indicated by asterisks. Cross sectional views of the originally proposed and modified structures are shown in Figure 2.1.

The originally proposed 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. For process verification purposes we have resolved to use square cells shaped from Czochralski crystals 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 it 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

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) Surface preparation

2)* Print diffusion masking dielectric on back*

3)* Fire diffusion masking dielectric on back*

4) Apply front polymer dopant

5) Diffusion

5a)*Strip diffusion oxide

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

11b)*AR coat

12) Test cells

*Steps where major modifications from original proposal have been introduced.

2.1a. Original Proposal

2.1b. Modified as of 7-1-78

Figure 2.1. Cross-sectional views showing cell structure as originally proposed and as subsequently modified.

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 diffusion 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. 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 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 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.

A spin-on diffusion source, Emulsitone N-250 has been selected. Spray-on and contact transfer application techniques have been evaluated and found to be satisfactory. As a further innovation, it was originally proposed that the diffusion oxide not be removed, but retained to serve as an antireflection coating. 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. 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. Requirements for the aluminum firing have been further defined during the third quarter.

At this point an additional printing and firing operation was introduced to locate dielectric isolation pads for the wrap-around contacts on the back aluminum. This was followed by printing solderable contacting pads on the back surface. During the second quarter silver contact pads on the aluminum back were found to be unsuitable because of galvanic corrosion effects. Tin applied by ultrasonic soldering techniques was found to be more satisfactory. The front metallization grids and wraparound conductors are then printed. For this we originally proposed using an aluminum thick film paste. 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 in understanding and improving the performance of screen printed silver front contacts.

2.2 TECHNICAL OVERVIEW OF MODULE DESIGN AND PROCESS SEQUENCE

The module design and selected process sequence are shown in Table 2.2. 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 second quarter, square cells based on 3 inch diameter Czochralski crystals were decided on as test vehicles for process verification in anticipation of larger square or rectangular sheet materials becoming available. The

Table 2.2

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

$\eta_m = 12\%$

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)

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 have 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 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.

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. Silicone is still a leading candidate, however acrylic and polyurethane candidates have been added for evaluation as possibly being more cost effective.

3.0 TECHNICAL DISCUSSION

3.1 JUNCTION FORMATION

3.1.1 Diffusion Masking Dielectric

Based on our previous work⁽¹⁾, two glass series, a titania precipitated series (5E) and a baria-magnesia borosilicate series (7E) were selected for further effort.

Series 5 - Titania Precipitated Glass

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 therefore highly stable when subjected to thermal excursions, and should be an excellent system for the masking dielectric.

The initial evaluation of this material suggested effectiveness as a diffusion barrier. Attempts to integrate its use in the fabrication of solar cells using diffusion from a polymeric source and printed aluminum back contacts were unsuccessful. In order to identify the nature of the problem, a dielectric mix was developed in which silica was substituted for titania, which was considered to be a possible contaminant. In order to further reduce the possibility of contaminants, one lot of the new paste was prepared from glass smelted in a platinum crucible instead of the usual clay crucible. Compositions of these glasses are given in Table 3.1.

Table 3.1

Series 5 Compositions

Oxide	5E-7	5E-8	5E-7-1	5E-7-1P ⁽³⁾
		<u>Equivalent</u>		
Na ₂ O	.271 ⁽¹⁾	.219	.270 ⁽¹⁾	.271 ⁽¹⁾
K ₂ O	.088	.093	.088	.088
CaO	.216	.234	.216	.216
Li ₂ O	.276 ⁽²⁾	.292	.276 ⁽²⁾	.276 ⁽²⁾
ZnO	<u>.150</u>	<u>.162</u>	<u>.150</u>	<u>.150</u>
Total	1.000	1.000	1.000	1.000
B ₂ O ₃	2.752	2.932	2.752	2.752
TiO ₂	1.393	1.489	-	-
SiO ₂	7.338	7.823	8.731	8.731
		<u>Mol Percent</u>		
Na ₂ O	2.16	1.65	2.16	2.16
K ₂ O	0.70	0.70	0.70	0.70
CaO	1.73	1.77	1.73	1.73
Li ₂ O	2.21	2.20	2.21	2.21
ZnO	1.20	1.22	1.20	1.20
B ₂ O ₃	22.05	22.14	22.05	22.05
TiO ₂	11.16	11.24	-	-
SiO ₂	58.78	59.07	69.94	69.94
Expansion Coefficient	5.2	5.2	3.5	3.5
(x 10 ⁻⁶ /°C)				

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

(3) Glass smelted in platinum crucible

Series 7 - Baria-Magnesia Borosilicate Glass

Series 7E was prepared to be free of alkali metal ions. Lead fluoride (PbF_2) was added to improve adhesion⁽¹⁾. Evaluation of composition 7-8-1A, formulated on the basis of previously reported fusion flow tests, indicated excessive refractoriness (underfiring). The series 7 glasses were further compounded to decrease maturation temperature and expansion coefficient. The compositions shown in Table 3.2 were compounded and evaluated. Maturing temperature of these coatings were between 700 and 750°C. The surfaces were free of bubbles. It was then discovered that the original difficulty was overfiring rather than underfiring. Therefore to obtain a higher maturing temperature (880°C) the refractory oxide content will be increased. Composition 7E-17 (Table 3.2) was compounded to increase the maturing temperature but has not yet been tested.

Cell Fabrication Experiments

Exploratory tests of the titania precipitated (Series 5) glasses were conducted during the previous quarter. In the first tests, wafers with strips of diffusion masking dielectric were submitted to a diffusion cycle using the Emulsitone N-250 phosphorus source. Examination of the underlying silicon by staining techniques and resistivity measurements after stripping the diffusion mask showed no evidence of phosphorus penetration.

Attempts were then made to integrate this mask into the process sequence:

Print and fire mask
Diffuse
Print and fire aluminum back

Cells produced with compositions 5E-7 and 5E-8 were very inferior. Tests of a reformulation in which the titania was replaced by silica (Composition 5E-7-1) were tested with equally dismal results. The use of a platinum crucible for the frit fabrication did not improve the result.

Table 3.2
COMPOSITION OF SERIES 7 DIFFUSION MASKING DIELECTRICS
(Equivalents)

Oxide	7E-8-1	7E-8-1A	7E-12	7E-13	7E-14	7E-15	7E-16	7E-17
BaO	0.260	0.253	0.403	0.285	0.285	0.253	0.270	0.253
ZnO	0.055	0.054	---	0.061	0.061	0.054	0.059	0.054
CaO	0.056	0.054	0.081	0.061	0.061	0.054	---	0.054
MgO	0.629	0.612	0.494	0.563	0.563	0.612	0.671	0.612
PbO	---	0.027	0.022	0.030	0.030	0.027	0.030	0.027
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al ₂ O ₃	---	---	---	---	---	---	---	0.300
B ₂ O ₃	0.506	0.492	0.397	0.619	0.780	0.550	0.539	0.492
SiO ₂	0.433	0.421	0.345	0.474	0.474	0.421	0.462	0.421

Compositional Changes

- 7E-12 In 7E-8-1-A, increased BaO to 0.500 equivalents, eliminated ZnO, increased CaO to 0.100 equivalents.
- 7E-13 In 7E-8-1-A, increased B₂O₃ to 0.550 equivalents, reduced MgO to 0.50 equivalents.
- 7E-14 In 7E-13, increased B₂O₃ to 0.780 equivalents.
- 7E-15 In 7E-8-1-A, increased B₂O₃ to 0.55 equivalents.
- 7E-16 In 7E-8-1-A, removed CaO.
- 7E-17 In 7E-8-1-A, added 0.3000 equivalents of Al₂O₃.

During the present quarter these cell fabrication experiments were repeated with some modification of process sequence and extended to include composition 7E-8-1. Two different process sequences were used as outlined in Table 3.3. The essential difference in the two sequences is the use of a printed aluminum back intermediate step in the second sequence.

The effects of potential titania, clay crucible and alkali metal contamination were investigated by fabricating cells using process 1 (no aluminum) and pastes 5E7, 5E7-1-P and 7E8-1. Cell characteristics at AM1 and 28°C are reported in Table 3.4. It should be noted that the 5 series samples were run as a group, while the 7 series units were processed at a subsequent date.

The data obtained in this series of experiments completely fail to support the hypothesis of contamination arising from the titania, clay crucible or alkali metal ions. In fact the best results were seen with the original 5E7 dielectric, with each attempt at refinement resulting in poorer characteristics. E-I curves for the cells with contact firing times of 20 seconds are shown in Figure 3.1. Although the best cells obtained here were relatively inferior, they were far superior to those obtained in the original evaluation. In that experiment the use of an aluminum back was included.

Cells were next fabricated using process sequences 1 and 2 (Table 3.3) and formulations 5E7 and 5E8. Cell characteristics at AM1 and 28°C are reported in Table 3.5. The major problem with curve shape in this experiment appeared to be very low shunt resistance. This was verified by estimating the shunt resistance using the dark reverse current on a number of cells. These estimates, also reported in Table 3.5, were all below 10 ohms in contrast to a value of 120 ohms or more obtained with silver thick film front and rear contacts.

Table 3.3

PROCESS SEQUENCES FOR EVALUATING
DIFFUSION MASKING DIELECTRICS

1	2
a) Print and dry diffusion dielectric	a) same
b) Fire diffusion dielectric (7 minutes @ 880°C)	b) same
c) Diffuse wafer (phosphine) (60 minutes at 850°C)	c) same
d) Back etch wafer (TFS A256 + 2% N diffusol)	d) Print aluminum, dry and fire (10 seconds at 900°C)
e) Remove dielectric with HF	e) Remove aluminum with concentrated HCl
f) Print front contact and dry	f) same
g) Print back contact and dry	g) same
h) Fire front and back contact (20 seconds at 700°C)	h) same

Table 3.4

Cell characteristics at AM1 and 28° for cells fabricated with exposure to diffusion masking dielectric during the diffusion step (Process Sequence 1, Table 3.3). Reported values are the averages of the number of cells in parenthesis.

Contact Firing Time (sec)	5E7	5E7-1 V_{OC} (mv)	5E7-1-P	7E8-1
10	596 (1)	597 (1)	-	-
15	593 (2)	592.5 (2)	558 (1)	-
20	594 (1)	587 (1)	581 (1)	585.7 (3)
25	594 (1)	587 (1)	581 (1)	588.6 (3)

	I_{SC} (mA)			
10	661 (1)	655 (1)	640 (1)	-
15	657.5 (2)	670 (2)	647.5 (2)	-
20	655 (1)	663 (1)	633 (1)	660.3 (3)
25	682 (1)	677 (1)	638 (1)	671 (3)

	I_{475} (mA)			
10	421 (1)	373 (1)	355 (1)	-
15	565.5 (2)	535.5 (2)	432 (2)	-
20	540 (1)	485 (1)	370 (1)	465.3 (3)
25	592 (1)	519 (1)	202 (1)	537.3 (3)

Table 3.5

Effect of aluminum firing on cell characteristics of cells fabricated with exposure to diffusion masking dielectric during the diffusion step (Table 3). Reported values are the averages for the number of cells given in parentheses.

Contact Firing Time (sec)	5E7		5E8	
	Process 1	Process 2	Process 1	Process 2
	V_{OC} -mv			
20	561.0 (5)	448.4 (5)	583.8 (5)	546.3 (3)
25	568.7 (3)	448.4 (5)	576.7 (3)	575.7 (3)
	I_{SC} (mA)			
20	674.4 (5)	649.0 (5)	666.6 (5)	662.0 (3)
25	659.0 (3)	613.7 (3)	651.3 (3)	655.0 (3)
	I_{475} (mA)			
20	312.2 (5)	228.4 (5)	502.8 (5)	263.3 (3)
25	348.7 (3)	125.0 (3)	458.0 (3)	381.7 (3)
	R_{SH} Ohms			
20	3.0 (1)	1.2 (2)		
25	2.1 (1)		4.4 (3)	

In this experiment the introduction of aluminum back contacts into the process sequence had an adverse impact on the solar cell characteristics. However, the cells fabricated using the 5-E-7 dielectric and process sequence 1 were decidedly inferior to those obtained in the previous experiment. This result suggests the presence of an unidentified process variable which is not being controlled.

The cells fabricated with 5-E-8 dielectric and aluminum backs were edge etched in order to determine the extent to which additional leakage might be attributed to edge shunting. Cell characteristics before and after edge etching are compared in Table 3.6 with those for cells fabricated from the same paste without the aluminum back (process sequence 1). The edge etching process substantially improved the performance of the cells fired for 20 seconds. Examination of the individual cell data showed that the poor result for the 25 second firing time group was due to one cell whose current at load dropped from 330 mA to 149 mA during the edge etching process.

3.1.2 Aluminum Back Contact

Previous experience has shown that best P+ back field effects are obtained with aluminum pastes when fired at rather high temperatures for short time periods with steep heating and cooling temperature ramps⁽²⁾. These requirements can be understood by considering the aluminum-silicon phase diagram (Figure 3.2). What is desired is to obtain a uniform layer of heavily aluminum doped silicon on the back surface of the wafer.

When the printed wafer is heated to the temperature range 750°-900°C, the aluminum melts and can dissolve silicon to the extent of about 22 to 34 atomic percent. Upon subsequent cooling, silicon will be precipitated which is heavily doped (saturated) with aluminum. As the system cools the silicon content of the melt decreases until the eutectic composition and temperature is reached, where an intimate mixture of aluminum and silicon phases forms.

Table 3.6

Effect of edge etching on cell characteristics of aluminum back contact cells. Reported data are averages for the number of cells indicated in parentheses.

Process Sequence *	2	2	1
Edge Treatment	None	Etched	None
Contact Firing Time	V_{OC} (mV)		
20 sec	546.3 (3)	584.3 (3)	583.8 (5)
25	575.7 (3)	560.7 (3)	576.7 (3)
	I_{SC} (mA)		
20 sec	662.0 (3)	570.0 (3)	666.6 (5)
25	655.0 (3)	666.7 (3)	651.3 (3)
	I_{475} (mA)		
20 sec	263.3 (3)	482.7 (3)	502.8 (5)
25	381.7 (3)	342.7 (3)	458.0 (3)

*See Table 3.3

Figure 3.2

SILICON-ALUMINUM PHASE DIAGRAM⁽³⁾

With rapid heating and cooling, only the aluminum adjacent to the interface will be saturated. There will be a composition gradient into the aluminum with the silicon concentration decreasing with increasing distance from the interface. Thus the natural tendency of the silicon to deposit epitaxially on the readily available solid silicon surface at the interface rather than the formation of new silicon nuclei will be reinforced. The concentration gradient will also minimize the formation of liquid layer instability due to depletion of the silicon in the liquid as the interface advances with falling temperature.

The rapid heating will also tend to result in a smoother interface. The 111 surfaces of silicon are thermodynamically favored in contact with molten aluminum. By heating rapidly the aluminum adjacent to the interface is maintained in a superheated (undersaturated) condition which results in kinetic effects dominating to produce a relatively smoother surface on the 100 oriented wafer surface. This effect will also minimize local excess penetration of the molten aluminum, and subsequently formed P+ layer, at localized inhomogeneities or imperfections in the silicon crystal.

During this reporting period a major effort was concentrated on identifying degradation mechanisms associated with firing aluminum back contacts. Leakage currents (low shunt resistance) were identified as a major source of cell performance degradation introduced by this aluminum process step.

Two different process sequences (identified in Table 3.7) were used in order to evaluate different interactions. Two sets of wafers were processed, one using Englehard 3484A aluminum paste and one using a paste made by mixing Alcoa #1401 aluminum powder with a vehicle designated as V-13. The formulation of V-13 is as follows:

Table 3.7

PROCESS SEQUENCES FOR EVALUATING
ALUMINUM BACK CONTACTS

Parts by Weight

α Terpinol	46 to 45	1/1 ratio	Total = 100 parts by weight
Butyl Carbitol Acetate	46 to 45		
Ethyl Cellulose (N-14)	8 to 10		
Tixatrol ST	1.5		

Sources for the above materials are as follows:

α Terpinol and Butyl Carbitol Acetate	MC/B Manufacturing Chemists 2121 South Leo Street Los Angeles, CA
Ethyl Cellulose (N-14)	Hercules, Incorporated 500 South Lafayette Place Los Angeles, CA
Thixatrol ST	NL Industries, Incorporated Industrial Chemical Division Highstown, NJ 08520

- a) To the mixture of α terpinol and butyl carbitol acetate at 70°C add ethyl cellulose. Stir constantly until dissolved..
- b) Cool to room temperature.
- c) Disperse Thixatrol ST in above mixture using a Waring blender. Do not allow temperature of mix during blending to exceed 50°C.
- d) Age for 16 hours at room temperature before use.

Cell performance parameters are summarized in Table 3.8. Series resistance and shunt resistance measurements were made on three or four cells out of each group. The observed ranges of these parameters are reported in Table 3.9.

From these data it can be seen that attainment of P+ backfield as measured by V_{oc} is somewhat erratic (compare V_{oc} for Sets 1 and 2). This is a manifestation of the effects of paste characteristics on the appropriate firing conditions.

Table 3.8

Cell performance parameters for aluminum back contact experiments, sintered 10 sec. @ 900°C in air atmosphere Data reported are $\bar{X}$, (n), σ_X .

See Table 3.7 for process description.

V_{OC} (mV)

Process 1

Process 2

1, Engelhard	595.3 (19) 1.40	602.1 (17) 1.59
2, Alcoa 1401 + V-13	594.9 (19) 1.67	595.8 (15) 1.47

I_{SC} (mA)

1	650.4 (19) 7.23	686.2 (17) 8.02
2	652.2 (19) 6.63	662.4 (15) 11.3

I_{475} (mA)

Set 1	586.9 (19) 13.7	624.2 (17) 8.46
2	588.9 (19) 18.4	596.1 (15) 23.13

Table 3.9

Series and shunt resistance parameters for
aluminum back contact experiments, sintered
10 seconds at 900°C in air atmosphere

Paste	Process 1		Process 2	
	R_s - ohms	R_{sh} - ohms	R_s - ohms	R_{sh} - ohms
1. Englehard 3484A	.068 - .080	12.8 - 38	.044 - .080	14.3 - 28.6
2. Alcoa 1401 + V-13	.070 - .165	159 - 370	.039 - .081	14 - 47

Secondly, introduction of the aluminum paste back contact is accompanied by a substantial drop in shunt resistance (to about 15-50 ohms as compared with a normal range of 100-500 ohms for silver paste back contacts). However, it is somewhat disconcerting that one of the control samples (Set 1, Process 1) also had a low shunt resistance, indicating the possibility that some unknown and uncontrolled variable is having an effect. Data reported in the preceding section (Table 3.6) suggest that some of the shunting effects are due to edge contamination, and if this can be suppressed, the situation may be somewhat alleviated. Despite the degradation in shunting resistance, the output current at load point is enhanced by about 6% if the P+ back field effect is achieved (Set 1). Even when the effect is not achieved, the aluminum paste back contact is effective for cost reduction without loss of output power (Set 2).

The specific requirements for these glasses are as follows:

- (1) Maturation temperature between 550 and 650°C.
- (2) Thermal expansion coefficient between 3.9 and $4.6 \times 10^{-6}/^{\circ}\text{C}$.
- (3) Freedom from bubbles and pinholes.

Four families of glasses have been explored for this application. These families are specifically (1) phosphate glasses (Series 4I), (2) germania/tantalum and silica/tantalum glasses (Series 6I), (3) baria-magnesia borosilicate glasses (Series 7I) and (4) modified titania precipitated glasses (Series 9I).

Series 4I Glasses

Series 4I-1 through 4I-11, all exhibited lack of maturity at temperatures as high as 880°C. Additionally, the calculated expansion coefficients were considered too high as shown in Table 3.10. These compositions were altered in Series 4I-12 through 4I-15 to reduce maturation temperature and expansion as shown in Table 3.11. These coatings matured between 650 and 700°C, but still had excessively large expansion coefficients. Moreover, they were found to be moisture sensitive and for these reasons were dropped from further consideration.

Series 6I Glasses

The starting composition of the germania-tantalum series (Table 3.12) was applied to silicon and fired at 650°C. This composition was deemed as too refractory. Increasing the germania content to 1.000 equivalents did not reduce the maturing temperature. Substitution of LiF for the Li_2O resulted in bubble formations without affecting the maturation temperature. It was decided that this coating system be set aside due to its refractory characteristics, and the analogous silica series explored.

Table 3.10

TYPICAL COMPOSITIONS OF INITIAL SERIES 4 GLASSES

Oxide	4I-1	4I-3	4I-7	4I-8
	Equivalents			
Li ₂ O	←→	0.485	←→	→
K ₂ O	←→	0.515	←→	→
Total	←→	1.000	←→	→
P ₂ O ₅	←→	2.976	←→	→
B ₂ O ₃	---	---	1.250	1.250
SiO ₂	---	1.000	1.250	0.500
Mol Percent				
Li ₂ O	12.20	9.75	7.49	8.47
K ₂ O	12.95	10.35	7.95	8.99
P ₂ O ₅	74.85	59.81	45.95	51.97
B ₂ O ₃	---	---	19.30	21.83
SiO ₂	---	20.10	19.30	8.73
Expansion Coefficient (x10 ⁻⁶ /°C)				
	9.8	9.0	7.7	8.1

Table 3.11

COMPOSITIONS OF REVISED SERIES 4 GLASSES

Oxides	4I-12	4I-13	4I-14	4I-15
	Equivalents			
Na ₂ O	←→	0.500	←→	→
Li ₂ O	←→	0.150	←→	→
NaF	←→	0.350	←→	→
Total	←→	1.000	←→	→
P ₂ O ₅	←→	0.200	←→	→
B ₂ O ₃	0.500	1.500	2.000	2.500
SiO ₂	0.800	0.800	1.000	1.200
Mol Percent				
Na ₂ O	20.00	14.29	11.90	10.20
Li ₂ O	6.00	4.29	3.57	3.06
NaF	14.00	10.00	8.33	7.14
P ₂ O ₅	8.00	5.71	4.76	4.08
B ₂ O ₃	20.00	42.86	47.62	51.02
SiO ₂	32.00	22.86	23.81	24.49
Expansion Coefficient (x10 ⁻⁶ /°C)				
	---	8.3	7.1	6.2

Table 3.12

COMPOSITIONS OF SERIES 6I-1 GERMANIA-TANTALUM GLASSES

Oxide	6I-1	6I-1-1	6I-1-2
	Equivalents		
Li ₂ O	0.740	0.740	--- except that LiF for Li ₂ O.
ZnO	0.360	0.260	
Al ₂ O ₃	0.043	0.043	
B ₂ O ₃	4.277	4.277	
Ta ₂ O ₅	0.039	0.039	
GeO ₂	0.600	1.000	
P ₂ O ₅	---	---	
Mol Percent			
Li ₂ O	12.41	11.63	Same as 6I-1 was substituted ---
ZnO	4.39	4.09	
Al ₂ O ₃	0.71	0.68	
B ₂ O ₃	71.73	67.26	
Ta ₂ O ₅	0.66	0.61	
GeO ₂	10.10	15.72	
P ₂ O ₅	---	---	

The silica-tantalum glasses, as shown in Table 3.13 are germania-free borosilicates with Li_2O and Ta_2O_5 . Composition 6I-2-2 was judged best in obtaining maturity at temperatures between 650 and 700°C. Variations in the composition of the silica-tantalum glasses were made to obtain glasses which were (1) smooth and glossy when fired and (2) compositions free of Ta_2O_5 . All of the glasses exhibited bubble formation when compounded free of Ta_2O_5 . The addition of 5 parts of PbF_2 per 100 parts by weight to the as ground glass powder did not reduce bubble formation. The effects of these variations are summarized in Table 3.14.

Because of the problems with the silica-tantalum series, the composition of the original germania-tantalum series was substantially altered by decreasing B_2O_3 and increasing GeO_2 and Ta_2O_5 in an attempt to overcome its refractory character (Table 3.15). The initial composition of this series (6I-3) resulted in an under-fired condition at 700°C. However this condition was remedied by increasing the B_2O_3 content to 4.500 equivalents. The elimination of Ta_2O_5 in this system caused bubbling of the surface. The effects of the compositional variations are summarized in Table 3.16.

One additional compositional variant of the germania-tantalum glasses (Series 6I-4) was investigated (Table 3.17), extending the compositional modifications of Series 6I-3 still further. This coating system exhibited a high wetting angle and an overfired condition. The germania content of 6I-4 was reduced appreciably (6I-4-1) without affecting the wetting angle, but maturation occurred at a firing temperature of 650°C. Elimination of Ta_2O_5 resulted in bubble formation upon application to silicon and firing at 650°C. The effects of compositional variations within the 6I-4 series is summarized in Table 3.18.

Table 3.13

COMPOSITION OF SERIES 6I-2 SILICA/TANTALUM GLASSES

Oxides	6I-2	6I-2-1	6I-2-2	6I-2-3	6I-2-4	6I-2-5	6I-2-6
	Equivalents						
Li ₂ O	0.575	0.575	0.605	0.575 ⁽¹⁾	0.575 ⁽¹⁾	0.575 ⁽¹⁾	0.605
ZnO	0.425	0.425	0.395	0.425	0.425	0.425	0.395
Al ₂ O ₃	0.282	0.282	0.186	0.282	0.282	0.282	0.186
B ₂ O ₃	4.954	5.400	4.608	4.954	4.954	4.954	4.608
Ta ₂ O ₅	0.103	0.103	0.096	0.103	---	---	---
SiO ₂	1.724	1.724	1.395	1.724	1.724	1.724	1.395
P ₂ O ₅	---	---	---	---	---	0.103	---
Mol Percent							
Li ₂ O	7.13	6.76	8.30	7.13	7.22	7.13	8.42
ZnO	5.27	4.99	5.42	5.27	5.34	5.27	5.49
Al ₂ O ₃	3.50	3.31	2.55	3.50	3.54	3.50	2.59
B ₂ O ₃	61.44	63.46	63.25	61.44	62.24	61.44	64.10
Ta ₂ O ₅	1.28	1.21	1.32	1.28	---	---	---
SiO ₂	21.38	20.26	19.15	21.38	21.66	21.38	19.40
P ₂ O ₅	---	---	---	---	---	1.28	---

Table 3.14

COMPOSITIONAL CHANGES IN 6I-2 SERIES

Coating	Changes	Remarks
6I-2-1	Increased B_2O_3 content of 6I-2 to 5.400 equivalents.	Refractory characteristics not eliminated
6I-2-2	Increased Li_2O content to 0.65 equivalents. Decreased Al_2O_3 content to 0.200 equivalents. Reduced SiO_2 to 1.500 equivalents.	Matured to a smooth coating at $700^{\circ}C$. Under fired at $650^{\circ}C$.
6I-2-3	Substituted LiF for Li_2O in 6I-2.	Formed bubbles on surface.
6I-2-4	Eliminated Ta_2O_5 from 6I-2-3.	Formed bubbles.
6I-2-5	Substituted P_2O_5 for Ta_2O_5 in 6I-2-3.	Formed bubbles

Table 3.15

COMPOSITION OF SERIES 6I-3 GERMANIA/TANTALUM GLASSES

	6I-1	6I-3	6I-3-1	6I-3-2	6I-3-3	6I-3-4	6I-3-5
Oxide	Equivalents						
Li ₂ O	0.740	0.448	0.448	cept that LiF was Li ₂ O	0.448 ⁽¹⁾	0.448 ⁽¹⁾	0.448
ZnO	0.260	0.552	0.552		0.552	0.552	0.552
Al ₂ O ₃	0.043	0.220	0.220		0.220	0.220	0.220
B ₂ O ₃	4.277	3.605	4.500		3.592	3.592	4.500
Ta ₂ O ₅	0.039	0.081	0.081		---	---	---
GeO ₂	0.600	0.771	0.771		0.771	0.771	0.771
P ₂ O ₅	---	---			---	0.081	---
Mol Percent							
Li ₂ O	12.41	7.89	6.82	Same as 6I-3 ex- substituted for	8.02	7.91	6.90
ZnO	4.39	9.72	3.40		9.89	9.75	8.50
Al ₂ O ₃	0.71	3.88	3.35		3.94	3.88	3.39
B ₂ O ₃	71.73	63.50	63.47		64.33	63.42	69.33
Ta ₂ O ₅	0.66	1.43	1.23		---	---	---
GeO ₂	10.10	13.58	11.73		13.81	13.61	11.878
P ₂ O ₅	---	---	---		---	1.43	---

(1) Li₂O added as LiF

Table 3.16

COMPOSITION CHANGES IN 6I-3 SERIES

Coating	Changes	Remarks
6I-3-1	Increased B_2O_3 content of 6I-3 to 4.500 equivalents	Good maturation between 650 and 700°C.
6I-3-2	Substituted LiF for Li_2O in 6I-3	Bubbles formed, good coating.
6I-3-3	Eliminated Ta_2O_5 from 6I-3-2.	Formed coating with high quantity of bubbles at 650 and 700°C.
6I-3-4	Substituted P_2O_5 for Ta_2O_5 in 6I-3-2.	Formed very rough surface at 650 and 700°C
6I-3-5	Eliminated Ta_2O_5 in 6I-3-1	Excessive bubbles

Table 3.17

	6I-1	6I-3	5-I-4	6I-4-1	6I-4-2	6I-4-3	6I-4-4
Oxide	Equivalents						
Li ₂ O	0.740	0.448	0.575	0.575	that LiF was sub-	0.575 ⁽¹⁾	0.575 ⁽¹⁾
ZnO	0.260	0.552	0.425	0.425		0.425	0.425
Al ₂ O ₃	0.043	0.220	0.563	0.563		0.563	0.563
B ₂ O ₃	4.277	3.605	2.891	2.891		2.874	2.874
Ta ₂ O ₅	0.039	0.081	0.103	0.103		---	---
GeO ₂	0.600	0.771	2.086	1.500		2.086	2.086
P ₂ O ₅	---	---	---	---		---	0.052
Mol Percent							
Li ₂ O	12.47	7.89	8.66	9.49	Same as 6I-4 except stituted for Li ₂ O	8.81	8.75
ZnO	4.39	9.72	6.40	7.02		6.52	6.46
Al ₂ O ₃	0.71	3.88	8.48	9.30		8.63	8.55
B ₂ O ₃	71.73	63.50	43.52	47.73		44.06	43.71
Ta ₂ O ₅	0.66	1.43	1.55	1.70		---	---
GeO ₂	10.10	13.58	31.40	24.76		31.98	31.73
P ₂ O ₅	---	---	---	---		---	0.79

(1) Li₂O added as LiF

Table 3.18

COMPOSITION CHANGES IN 6I-4 SERIES

Coating	Changes	Remarks
6I-4-1	Decreased GeO_2 content of 6I-4 to 1.500	Retained high wetting angle, but matured at 650°C
6I-4-2	Replaced Li_2O with LiF in 6I-4	Formed bubbles on surface
6I-4-3	Eliminated Ta_2O_5 from 6I-4-2	Formed bubbles on surface
6I-4-4	Substituted P_2O_5 for Ta_2O_5 in 6I-4-2	Had bubbles, cracks and voids

A study of the fusion-flow characteristics of the Series 6 glasses was carried out. In this test 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 in the vertical position. The flow of the melted glass is measured to the nearest 0.5 mm. Positive results were obtained only with the compositions shown in Table 3.19.

In a further attempt to improve the bubble condition the most promising compositions 6I-2-2 and 6I-3-1 were modified by increasing the B₂O₃ content (Table 3.20). This result was not successful with the compositions 6I-X-6 and 6I-X-7 (X = 2 or 3), however some reduction in bubble formation was achieved by complete elimination of Al₂O₃ (6I-X-8). The effect of the compositional variations are summarized in Table 3-21.

The tendency to form bubbles was reduced by dry grinding of 6I-2-2 and 6I-3-1. These coatings matured when fired at 650° for seven minutes. Coatings of 6I-2-2 and 6I-3-3, when ground dry, exhibited increasing bubble size as a function of temperature when fired at 600, 650 and 700°C for seven minutes.

Series 7I Glasses

In view of the excellent firing obtained with baria-magnesia borosilicate Series 7E composition as a diffusion mask, the compositions were altered in an attempt to reduce the fusion temperatures from 850 to 650°C. Compositions 7I-1 and 7I-2 (Table 3.22) did not flow during fusion flow tests at 750 and 850°C.

Table 3.19

FUSION FLOW CHARACTERISTICS OF SERIES 6 GLASSES

Series Number	Temp. (°C)	Time ⁽¹⁾ (min)	Flow Length (mm)
6I-3-2	700	4	17.0
6I-3-2	700	7	21.5
6I-3-2	750	4	26.5
6I-4-3	750	4	24.0
6I-4-2	700	7	20.0
6I-4-2	750	4	23.5

(1) Time in the vertical position. All samples held 1-1/2 minutes in the horizontal position.

Table 3.20

COMPOSITIONS OF MODIFIED 6I-2-2 AND 5I-3-1
SILICA-TANTALUM AND GERMANIA-TANTALUM GLASSES

Oxides	6I-2-2	6I-2-6	6I-2-7	6I-2-8	6I-3-1	6I-3-6	6I-3-7	6I-3-8
	Equivalents		except that as LiF instead	Equivalents			except that as LiF instead	
Li ₂ O	0.605	0.605		0.605	0.448	0.448		0.448
ZnO	0.395	0.395		0.395	0.552	0.552		0.552
Al ₂ O ₃	0.186	0.100		---	0.220	0.220		---
B ₂ O ₃	4.608	5.000		4.795	4.500	5.500		4.722
Ta ₂ O ₅	0.096	0.096		0.096	0.081	0.081		0.081
SiO ₂	1.395	1.200		1.395	---	---		0.771
GeO ₂	---	---		---	0.771	0.771		0.771
			MOL PERCENT					
Li ₂ O	8.30	8.18	Same as 6I-3-6 Li ₂ O introduced of Li ₂ CO ₃	8.30	6.82	5.92	Same as 6I-3-6 Li ₂ O introduced of Li ₂ CO ₃ .	6.82
ZnO	5.42	5.34		5.42	8.40	7.29		8.40
Al ₂ O ₃	2.55	1.35		---	3.55	2.91		---
B ₂ O ₃	63.25	67.60		65.81	68.47	72.63		71.83
Ta ₂ O ₅	1.32	1.30		1.32	1.23	1.07		1.23
SiO ₂	19.15	16.22		0.16	---	---		---
GeO ₂	---	---		---	11.73	10.18		11.71

Table 3.21

COMPOSITION CHANGES IN 6I-2-2 AND 6I-3-1 GLASSES

Coating	Changes	Remarks
6I-2-6	Increased B_2O_3 content of 6I-2-2 to 5.000 eq.	No effect on bubble formation
6I-2-7	In 6I-2-6, replaced Li_2CO_3 with LiF	No effect on bubble formation
6I-2-8	In 6I-2-2, replaced Al_2O_3 with B_2O_3	Reduced bubble formation
6I-3-6	Increased B_2O_3 Content of 6I-3-2 to 5.500 eq.	No effect on bubble formation
6I-3-7	In 6I-3-6, replaced Li_2CO_3 with LiF	No effect on bubble formation
6I-3-8	In 6I-3-2, replaced Al_2O_3 with B_2O_3	Reduced bubble formation

Table 3.22

COMPOSITIONS OF BARIA-MAGNESIA
BOROSILICATE GLASSES MODIFIED FOR LOWER
MATURATION TEMPERATURE

	7E-8-1	7I-1	7I-2
Oxide	Equivalents		
BaO	0.260	0.714	0.714
ZnO	0.055	0.143	---
CaO	0.056	0.143	0.143
MgO	0.629	---	---
PbO	---	---	0.143
Total	1.000	1.000	1.000
B ₂ O ₃	0.506	2.237	2.237
SiO ₂	0.433	1.524	1.524
	Mol Percent		
BaO	13.41	15.00	15.00
ZnO	2.85	3.00	3.00
CaO	2.89	3.00	---
MgO	32.43	-	3.00
PbO	---		
B ₂ O ₃	26.09	46.99	46.99
SiO ₂	22.32	32.01	32.01

Series 9I

The study of this series was initiated to reduce the maturing temperature of Series 5E (diffusion mask dielectric) from 880 to 650°C. Compositions 9I-1 through 9I-5 (Table 3.23) were evaluated in this report period. The compositional changes made in this series are summarized in Table 3.24.

Good maturity was obtained in coating 9I-4 at 700°C. As the calculated expansion coefficient of this coating is too large ($6.8 \times 10^{-6}/^{\circ}\text{C}$), the B_2O_3 and SiO_2 were increased with negative effects on the maturation temperature.

Coatings 9I-6 through 9I-8 were smelted trying to improve these characteristics. Although some success has been achieved (Table 3.24), the desired goal has not been reached.

As expansion is reduced by increasing the B_2O_3 and SiO_2 , maturing temperature increases. It is planned to alter the compositions by additions of lithia until a maturing temperature of 550°C is reached. This procedure will increase the thermal expansion. To offset this trend, B_2O_3 will be substituted for Li_2O in small increments to reduce the expansion. On a normalized weight percent basis the expansion contribution of B_2O_3 is 1/120 that of lithia.

Table 3.23

COMPOSITIONS OF SERIES 9 ISOLATION DIELECTRICS

	5E-7	9I-1	9I-2	9I-3	9I-4	9I-5	9I-6	9I-7	9I-8
Oxide	Equivalents								
Na ₂ O	.270 ⁽¹⁾	.270	.270	.169	.149	.231	.169	.270	.157
K ₂ O	.088	.088	.088	.055	.049	.075	.056	.088	.052
CaO	.216	.216	.216	.135	.119	.184	---	.216	---
Li ₂ O	.276 ⁽²⁾	.276	.276	.173	.153	.236	.174	.276	.232
ZnO	.150	.150	.150	---	---	---	---	.150	---
PbO	---	---	---	.469	.530	.273	.602	---	.559
B ₂ O ₃	2.752	2.752	2.752	2.313	2.485	3.843	3.405	3.500	3.162
TiO ₂	1.393	---	---	---	---	---	---	---	---
SiO ₂	7.338	7.338	5.000	2.313	1.545	3.843	1.754	3.000	1.629
Mol Percent									
Na ₂ O	2.16	2.43	3.09	2.55	3.96	2.66			
K ₂ O	0.70	0.79	1.01	0.83	0.97	0.86			
CaO	1.73	1.95	2.47	2.04	2.37	2.12			
Li ₂ O	2.21	2.49	3.15	2.61	3.04	2.72			
ZnO	1.20	1.35	1.71	--	--	--			
PbO	--	--	--	7.08	10.54	3.14			
B ₂ O ₃	22.05	24.82	31.44	42.45	49.40	44.24			
TiO ₂	11.16	--	--	--	--	--			
SiO ₂	58.78	66.17	57.13	42.45	30.72	44.24			

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

Table 3.24

COMPOSITION CHANGES IN SERIES 9 GLASSES

Coating	Changes	Remarks
9I-1	TiO ₂ eliminated from 5E7,	No fusion at 750°C
9I-2	Decrease SiO ₂ to 5.000 Eq.	No fusion at 750°C
9I-3	Eliminated ZnO, added PbO, further decrease in SiO ₂	No fusion at 750°C
9I-4	Increased PbO, decreased SiO ₂	Maturation and fusion flow at 700°C
9I-5	Decreased PbO to .273 Eq., increased B ₂ O ₃ and SiO ₂	No fusion at 750°C
9I-6	Eliminated CaO from 9I-4, Increased B ₂ O ₃	Expansion coef. reduced from 6.8 to $5.9 \times 10^{-6}/^{\circ}\text{C}$
9I-7	Increased B ₂ O ₃ in 9I-2 and decreased SiO ₂	Refractory, no fusion
9I-8	Increased LiO ₂ in 9I-6	Maturing temperature reduced, expansion coefficient $6.1 \times 10^{-6}/^{\circ}\text{C}$

Different types of silver paste front metallization produce various qualities of solar cells. The reasons for this variation are unclear. As an initial step into the investigation of the silver paste-silicon interaction, solar cells were produced with four types of silver paste. I-V curves for best cells produced from these pastes are shown in Figures 3.3 through 3.6. The metallization firing conditions and paste identification are given on the curves.

The silver in the paste does not melt during the sintering treatment, but the glass frit does melt. The major interaction with the silicon will be with the frit, not the silver. In order to investigate this interaction, the silver was removed with a dilute solution of hydrogen peroxide. Fluorescent analysis with the use of a SEM revealed the basic composition of the glass frit that remained after etching. The elements and intensities of the fluorescent radiation observed in the four types of paste are given in Table 3.25; light elements (boron and lithium) which might be in these pastes cannot be detected by this method. The pastes having a larger percentage of aluminum appear to have more shunting. The pastes that did not have any aluminum gave the best I-V curve but did not have the adherence necessary for good metallization.

SEM micrographs of the glass frit on the silicon's surface appear to be very similar for all pastes. The glass frit flows during the sintering process forming structural networks across the texture surface. The Dupont 7095 conductive silver paste flows very well at 700°C and forms a continuous layer of frit under the silver grid contacts (Figure 3.7). There does not appear to be any degradation of the textured surface. The Electrosience 590 and Electrosience 590 with 2% Emulsitone #733 (Sb dopant) does not flow as well as the Dupont 7095. The frit forms networks across pyramids with areas free of frit. The pyramids appear to have spots growing on

Figure 3.4. I-V curve for solar cell made with ESL type 590 ink fired for 25 seconds at 700°C, no AR coating, AM1, 28°C.

Table 3.25

RELATIVE FLUORESCENCE INTENSITIES OF ELEMENTS
PRESENT IN FRITS OF SILVER CONDUCTIVE PASTES

<u>Elements and Emission Lines</u>	<u>Dupont 7095</u>	<u>Electroscience Type 590</u>	<u>Electroscience 590 + 2% Emulsitone 733</u>	<u>EMCA Ag 92</u>
Pb M_{α} (2)	10	10	10	10
Al K_{α}	43	19	9	-0-
P K_{α}	-0-	41	41	-0-
K K_{α}	-0-	55	34	-0-
Si K_{α} (2)	47	95	77	111
Na K_{α} (2)	-0-	5	2	5
Ag L_{β}	20	22	20	22
Sb L_{α}	-0-	-0-	-0-	-0-

3.7a 2000X

3.7b 5000X

Figure 3.7. SEM of silver metallization contact area after removal of silver by dilute hydrogen peroxide. Dupont 7095 silver ink.

their sides, possibly frit (Figures 3.8 and 3.9). There does not appear to be any degradation of the textured surface. The EMCA Ag 92 appears to be the lowest melting frit forming the heaviest layer of frit on the textured surface (Figure 3.10). The frit appears to have flowed beyond the area of the silver grid contact and coated the adjacent textured surface with a thin layer of frit. The frit does not appear to have any detrimental effect on the silicon.

If one compares the I-V curves for the various commercial fritted silver pastes tested and the fluorescent analysis of these pastes, it appears that aluminum is a detrimental element. To determine whether aluminum-free frits produce high efficiency solar cells, three types of low melting frits were prepared (Table 3.26). Two percent by weight of these frits were added to a fritless silver paste. The efficiencies of cells made from these pastes are listed in Table 3.27. Figure 3.11 shows characteristic curves for cells made with paste based on Frit #2. All of these pastes produced very good cells and passed a tape pull test with Scotch Brand 600 tape; but when these pastes were soldered, the interconnect absorbed the silver on the contact, and the interconnections pulled off at a low load of 200 grams.

These frits developed at Spectrolab appear to satisfy the requirements for high efficiency solar cells, but they lack adherence after soldering. Additional development of these frits needs to be conducted in order to produce a silver paste that is adherent after soldering and produces a high efficiency solar cell.

3.4 X-RAY TOPOGRAPHIC ANALYSIS OF SILICON WAFERS WITH SCREEN PRINTED AND FIRED THICK FILMS

X-ray topographic analyses have been carried out on silicon terrestrial solar cell structures to determine the effect of various processing steps on the crystal perfection of the wafers. In particular, x-ray topographs have been made of:

3.8a. 2000X

3.8b. 5000X

Figure 3.8 SEM of silver metallization contact area after removal of silver by dilute hydrogen peroxide. Electrosience 590 silver ink.

3.9a. 2000X

3.9b. 5000X

Figure 3.9. SEM of silver metallization contact area after removal of silver by dilute hydrogen peroxide. Electrosience 590 silver ink + 2% Emulsitone 733 (Ag).

A

B

C

3.10a. 2000X

3.10b. 5000X

Figure 3.10. SEM of silver metallization contact area after removal of silver by dilute hydrogen peroxide. EMCA Ag 92 silver ink.

Table 3.26

COMPOSITION OF ALUMINUM-FREE GLASS FRITS

Frit No.	Weight Percent of Oxides			
	PbO	B_2O_3	P_2O_5	SiO_2
1.	93.81	4.65	--	1.54
2.	91.97	4.36	1.46	2.20
3.	95.56	4.44	2.68	--

Table 3.27

EFFICIENCIES OF DEVELOPED PASTES
Insolation: 100 mW/cm², no AR coating

Frit Identification and Temperature	Firing Time							
	10	15	20	25	30	40	50	60
1 (650°C)	--	--	11.5	--	13.3	12.3	12.8	11.9
1 (700°C)	13.3	12.8	12.2	13.0	12.0	--	--	--
2 (650°C)	--	--	13.5	--	13.1	12.9	12.9	12.2
2 (700°C)	13.6	12.8	12.5	12.7	11.9	--	--	--
3 (650°C)	--	--	12.9	--	13.3	12.9	12.6	11.2
3 (700°C)	13.1	12.9	12.4	12.9	12.6	--	--	--

- the Si wafer surface to assess the inherent perfection of the wafers,
- the front contact surface after thermal processing of the Ag-glass frit front metallization paste,
- the back Al contact surface after thermal processing, and
- the Si surface after application and thermal processing of the diffusion masking dielectric.

The topographic studies involve Lang reflection x-ray topography. The technique is illustrated in Figure 3.12. An x-ray beam from a small source is incident on the Si wafer through a narrow slit. The beam impinges the crystal at an angle adjusted to satisfy the Bragg conditions. A variable width diffracted beam slit is used to prevent extraneous reflections and incoherent radiation from reaching the photographic plate. The crystal and the photographic plate are then scanned together to produce a reflection topograph of the entire crystal face. If crystal imperfections are present, changes in contrast occur and the type of defect can be identified. The penetration depth of the 40 kV x-rays from a Ni target is of the order of 10 μm . Such penetration depth represents the region of interest in determining the effects of wafer surface treatment, thermal cycles and ohmic contacting.

3.4.1 Characterization

Wafer Perfection

The degree of crystal perfection for wafers having no ohmic contact or insulator processing is shown in the x-ray topograph of Figure 3.13. The circular wafer, 2 inches in diameter, has been cleaved in half and has a crack resulting from the cleaving. The wafer has no gross imperfections such as inclusions, low angle grain boundaries, slip

Figure 3.12
X-RAY CAMERA GEOMETRY

Figure 3.12. X-Ray Topograph of Si Wafer with No Contacts

or large-scale dislocation networks. Compared to commercially available Si, this material is of excellent crystal perfection.

Front Contact Area

The front contact area of the solar cell was examined by x-ray topography as shown in Figure 3.14. A wafer, to which the Ag-glass frit paste had been applied and fired to form the top contact grid, was treated to remove the grid. The grid was removed with 1:1 concentrated nitric acid:water after the grid had been fired for 20 seconds at 700°C in air. The x-ray topograph, Figure 3.14 shows a residual pattern of the ohmic contact grid, probably caused by local strain resulting from diffusion of constituents of the grid material during firing. It should be noted, however, that the application procedures and the firing cycle did not produce crystal dislocations or slip. The wafer also shows no evidence of warping. The dark horizontal lines are x-ray scanning artifacts, not a property of the wafer.

Back Contact Area

The back contact area of a solar cell was examined by x-ray topography. The Al contact material was applied uniformly to the wafer with the exception of an annular region around the periphery. The wafer was fired using a thermal cycle of:

10 seconds at 900°C in air
15 seconds at 600°C in air
20 seconds at 700°C in air

After firing, the aluminum was removed by etching in HCl at 60°C and the x-ray topograph of Figure 3.15 obtained. The wafer was cleaved in half resulting in a crack. In the region of Al alloying, there is evidence of regrowth regions when the wafer is examined by eye, but the x-ray topograph shows little structure in the Al alloying region with the exception of small circular regions sparsely distributed in the area. In the annular region where there was no Al

Figure 3.14. X-Ray Topograph of Front Contact Area, Si Solar Cell

Figure 3.15. X-Ray Topograph of Back Contact Area, Si Solar Cell

deposited, these features do not occur. The small circular regions were found to be regions having a thin regrowth layer associated with shallow penetrations by the molten aluminum.

Diffusion Mask

An insulation film for diffusion masking of the phosphorus diffusion is under investigation. The mask is required to mask the n+/P diffusion around the periphery of the wafer. To determine possible crystal damage from thermal processing of the deposited film on Si, a wafer with a bar pattern of masking film deposited on its surface was subjected to the following firing cycle:

30 minutes at 850°C in N₂
10 seconds at 900°C in air
15 seconds at 600°C in air
20 seconds at 700°C in air

The film was then removed with HF and the x-ray topograph of Figure 3.16 made. There is no evidence of damage induced in the wafer by the masking film bar pattern which was deposited in the central portion of the wafer (three bars each 25 mm in length and 3 mm, 2 mm and 1 mm width were deposited). The wafer does show extensive slip damage which is especially severe at the edge of the wafer. From experience with other Si device structures, it is not likely that the slip is caused by the deposited diffusion resist pattern or by handling. It should be pointed out that slip of this extent might be deleterious to the electrical terminal characteristics of the solar cells. The observed slip pattern resembles that sometimes found as a result of thermal stresses during crystal growth and may have been present in the original wafer.

Figure 3.16. X-Ray Topograph of Wafer used in Diffusion Mask Experiment

3.4.2 Summary

From the x-ray characterization performed to date, it is concluded that:

- The crystal perfection of the wafers is good.
- Front ohmic contact procedures do not produce significant crystal damage.
- Back contact processing does not produce extensive crystal damage, but there are alloy-induced circular defects associated with localized regions which are not dissolved into the molten aluminum.
- The firing of the diffusion mask film does not introduce noticeable crystal damage.
- Extensive slip was observed in one wafer and its cause is at present unknown.

3.5 BONDING AND BACK COATING

3.5.1 Materials Evaluation

The current status of candidate materials which have been considered for cell to superstrate bonding and for module back coating is reviewed in Tables 3.28 and 3.29 respectively.

Changes in the adhesive list from previous reports include addition of Dow Corning 96-083 and General Electric RTV 2144-131 to the list of candidate cell bonding materials, and the elimination of Shell Epon 828/Versamid 125 and Locktite 353 and 354. The two added candidates are silicones. The General Electric RTV 2144-131 was submitted as a material compounded to have essentially the same properties as General Electric RTV 615, but potentially available at significantly lower costs for high volume production. The Dow Corning 96-083 was selected for the potential advantage of the self priming.

The Epon 828/Versamid 125 system was not eliminated by tests directly related to its use as a cell bonding material, however results of an indirectly related test were unfavorable. Cells bonded to glass and also covered with approximately 1/8" coating of the material were subjected to thermocycle. This resulted in severe spalling of the coating which took with it not only the complete back metallization of the cells but also sections of the glass. Cracks also developed through the cross section of both cells and glass. However, the bond between cell front surfaces and glass was still completely intact. Evidently thin sections can be contained between glass and cells during thermocycling without developing severely damaging stresses. In this case with relatively more rigid, thicker sections, however, the large thermal expansion differential between the epoxy and both the glass and the cells caused severe shear stresses and the resultant spalling. On the other hand the thermal expansion differential between glass and silicon apparently is not great enough to cause

Table 3.28

STATUS OF CANDIDATE ADHESIVE MATERIALS

<u>MANUFACTURER</u>	<u>IDENTIFICATION</u>	<u>TYPE</u>	<u>COMMENTS</u>
Retained for further consideration:			
General Electric	RTV 515	Silicone RTV	
Dow Corning	96-033	Silicone Adhesive	
General Electric	RTV 2144-131	Silicone RTV	
Eliminated:			
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-560-4	Acrylic UV Cure	Poor temperature resistance
Rohm and Haas	Acryloid B-7	Acrylic, Thermo-plastic	Bubbles and unbonded areas, poor temperature resistance
Dow Corning	X3-6553	Silicone gel	Poor adhesion and permanently soft, tacky surface
Loctite	353	Acrylic UV cure	Loss of transmission $\lambda < 1000\text{m}\mu$ after UV exposure
Loctite	524	Acrylic heat cure	Loss of transmission $\lambda < 700\text{m}\mu$ after UV exposure
Shell	Epon 828/Versamid 125	Epoxy	High modulus, hydrolysis

Table 3.29

STATUS OF CANDIDATE PROTECTIVE COATING MATERIALS

<u>MANUFACTURER</u>	<u>IDENTIFICATION</u>	<u>TYPE</u>	<u>COMMENTS</u>
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Retained for Further Consideration:

Dow Corning	Q1-2577	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/ Mobay	QR-568/ Desmodure N75	Oxazolidine Acrylic/ Polyurethane	Delamination during thermal cycle
Rohm & Haas	Acryloid B-7	Acrylic	Poor adhesion
Dow Corning	R-4-3117	Silicone Coating	Poor adhesion

failure under the conditions of the test. Temperature excursions greater than the -40° to 90°C used, or cells larger than 2" diameter might develop damaging stresses. This combined with reported tendency for this material to undergo delayed long term failure due to hydrolysis were determining factors for its elimination.

The two Loctite adhesives were eliminated due to loss of transmission after exposure to UV radiation.

In the coatings list Dow Corning R4-3117 has been eliminated for poor adhesion and phase instability. Table 3.30 reviews the bond strength environmental exposure tests made to date on adhesive materials. Changes since the last report include re-test data for the apparently anomalous results from humidity exposure of the RTV 615/4120 glass-to-glass bond. The present values are much higher and appear to be more in line with other RTV 615/4120 bond strength test results.

New data includes results from test specimens bonded with RTV 615 using two additional primers, Dow Corning 1204 and Sylgard primer, and also data for cell to glass specimens bonded with the Loctite 353 and the Epon 828/Versamid 125 systems. These cell-to-glass specimens were tested after thermocycle exposure, and were included to simulate more closely actual service conditions with these higher modulus adhesives which could be expected to lead to thermal stresses.

Evaluation of adhesive bond strength for this program has been done primarily by pull testing of standard lap shear specimens bonded with the various candidate materials. With the stronger adhesives, these lap shear specimens may fail outside the test joint. Such failures frequently result from the tendency of the specimen to develop a torque at the joint during testing and usually involve mechanisms other than shear. Such failures are necessarily lower

Table 3-30

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

MATERIAL	AS BONDED			After THERMAL CYCLE -40°C to 100°C			AFTER HUMIDITY 95% @ 70°C		
	CELL TO CELL	CELL TO GLASS	GLASS TO GLASS	CELL TO CELL	CELL TO GLASS	GLASS TO GLASS	CELL TO CELL	CELL TO GLASS	GLASS TO GLASS
RTV 615	145		173	86		191	250		218
RTV 615/4120 Prim	330		250	195		238	310		264
RTV 615/4155 Prim			205			234			266
RTV 615/1204 Prim		56.5			121			57.0	
RTV 615/Sylgard Prim		290			473			420	
X3-6558	7.5		123	8.5		125	12.3		161
Loctite 524	812		448	566		428	369		280
Epon 828/Vers 121	744	740	284	272	764	273	436		278
Loctite 353 U.V.		527	572		766	591	468		453

than the true shear strength of the adhesive. Therefore a few specimens bonded with materials which had characteristically shown such failures were tested at JPL in a special fixture which supports them in such a way as to virtually eliminate all failure mechanisms except pure shear. These results are shown in Table 3.31.

With the high strength materials, failures were still not always in the test joint, but observed failure loads were generally much higher than could have been achieved with standard lap shear specimens. Therefore, these data more nearly approach the true shear strength of the corresponding materials even in cases of faulty failures.

Table 3.32 reviews the results of adhesion-environmental exposure tests made to date on candidate coating materials. 1 lb/in. has been set tentatively as the lower limit for peel strength, and any exposure test resulting in strengths below this level is considered cause for elimination of the corresponding candidate material. The data and also supplemental experience from handling the test specimens indicate that several of the materials may continue to cure during exposure, especially during thermal cycle, and exhibit improved properties compared to control specimens.

The tape adhesion tests, both as cured and 24 hour immersion, were performed within relatively short times after application (less than one week in all cases). In view of the continued cure of peel test specimens during exposure, (at least a week after application) improved tape test performance might also show up with additional aging after application.

Thermal Stresses in Bonded Solar Cell Panels

Stresses are induced in bonded silicon solar cells when there is a mismatch of thermal expansion between superstrate and silicon cell. A service temperature range of -40°C to $+90^{\circ}\text{C}$ results in differential expansion of plus or minus 65°C if cell adhesive is cured at 25°C .

Table 3.31

ADHESIVE SHEAR TESTS
SPECIAL SUPPORT FIXTURE
SHEAR STRENGTHS lbs/in²

(ALL BONDS CELL TO GLASS, AVERAGE OF TWO SPECIMENS)

<u>MATERIAL</u>	<u>AS BONDED</u>	<u>UV EXPOSURE</u>	<u>AFTER THERMOCYCLE -40° to 100°C</u>
RTV 615/4120 Primer	642	732	
RTV 615/No Primer	572	515	
Loctite 524	962*	1500*	
Epon 828 Versamid 125	1130*	770*	487*

*Failure not in test joint

Table 3.32

COATING MATERIALS EXPOSURE/ADHESION TESTS

MATERIAL	Peel Strength Tests (Pounds/inch) (Average Approx. 10 Specimens)						Tape Adhesion Test % Area Failed			
	Cured Film		Thermal Cycle		Humidity		Coating		H ₂ O 24 Hrs	
	Control		-40° to 100°C		95% 70°C		as Cured		Immersion	
	Cell	Glass	Cell	Glass	Cell	Glass	Cell	Glass	Cell	Glass
Q1-2577	6.0	2.2	6.4	2.0	1.8	1.2	100	100		
R4-3117	1.3	0.1	1.1	0.1	1.2	0.1	100	100		
X3-5035	1.7	1.8	1.9	1.9	1.1	1.0				
XB-1786 (with primer)		1.4								
PT469 Clear	> 2	> 2	> 2	> 2	> 2	> 2	pass	pass	pass	100%
Perma Resin	> 2	> 2	> 2	> 2	> 2		pass	pass	pass	100%
MIL-C-83286	> 2	2.5	> 2	2.4	> 2	> 2	pass	pass	pass	100%

From an engineering point of view it would seem that selecting a panel material of matching coefficient is the logical solution. However, those materials which have suitable matched coefficients are considerably more expensive than may be justified. Considerable cheaper panel materials may be used if resilient adhesives are used to limit the stresses caused by differential thermal expansion.

A simple stress analysis shows that the stress in silicon is a maximum at the center of the cell, and the maximum stress can be expressed as:

$$S_{\text{silicon}} = \frac{0.125 G (\alpha_{\text{panel}} - \alpha_{\text{silicon}}) \Delta T L^2}{(t_{\text{adhesive}}) (t_{\text{silicon}})} \quad (1)$$

- Where:
- G is the shear modulus of the adhesive (lbs/in²)
 - α_{panel} is coefficient of linear thermal expansion of the panel (in/in/°C)
 - α_{silicon} is coefficient of linear thermal expansion of silicon (in/in/°C)
 - t_{adhesive} is the thickness of the adhesive (in.)
 - t_{silicon} is the thickness of the silicon (in.)
 - ΔT is the temperature differential from the adhesive cure temperature
- and
- L is the lateral dimension of the silicon (in.).

Equation (1) shows that the stress introduced in the silicon is directly proportional to the shear modulus of the adhesive; therefore a low-modulus adhesive is helpful in reducing stresses. Stress is also directly proportional to the mismatch of coefficients; therefore the more expansive panel materials will require compensation in other parameters. Stress is inversely proportional to the thickness of the adhesive; therefore a greater thickness of adhesive may be required

for more expansive panels. Stress is inversely proportional to the thickness of the silicon; therefore economizing with thinner cells must be accompanied by compensation in other parameters. Finally, the stress level increases as the square of the cell width, requiring appropriate adjustments as cell size increases. Since the expansion coefficient of silicon is smaller than that of any practical panel materials, the silicon stress will be compression for temperatures below the adhesive cure temperature and tension for temperatures above the adhesive cure temperature. Elevated cure temperatures can therefore be used to limit the development of tensile stresses.

Stresses can be limited by using a low-modulus, resilient adhesive to bond cells to glass. However, differences in length produced by temperature change must be accommodated by shear strain in the adhesive. The shear strain in the adhesive will be a maximum at the edge of the cell (Figure 3.17), where it will be

$$\gamma = \delta / t_{\text{adhesive}} = \frac{L(\alpha_{\text{panel}} - \alpha_{\text{silicon}})\Delta T}{2 t_{\text{adhesive}}} \quad (2)$$

The variation of adhesive shear strain with cell dimensions and glue line thickness is shown in Figure 3.18 for cells bonded to soda-lime glass with a 65°C ΔT.

For General Electric RTV 615 ultimate uniaxial shear strain can be approximated at 90%. (Shear deformation data are not available. GE lists 925 psi as the tensile strength and 150% as the elongation. GE technical personnel offered that shear properties might be approximately 60% of tensile.) In view of the biaxial nature of the stress, the allowable shear strain should be much lower, perhaps 20-25%. For this adhesive Figure 3.18 suggests that the minimum glue

Figure 3.17. Shear strain in adhesive between silicon solar cell and panel

Figure 3.18. Effect of cell size and glue line thickness on adhesive shear strain, solar cells bonded to soda-lime glass with silicone RTV.

line thickness should be about 0.004 inches for cells having lateral dimensions of 4-5 inches. If an elevated cure temperature (150°C) is used and sub-zero environmental temperatures are expected, the minimum glue line thickness should be increased to .008 or .009 inches in order to accommodate the larger ΔT to the low end of the temperature cycle.

4.0 CONCLUSIONS

A substantial drop in cell shunt resistance is encountered in cells fabricated using printed aluminum back contacts in conjunction with printed silver contacts. A portion of the excess leakage current is associated with junction contamination and can be eliminated by cleaning procedures such as edge etching; however, a remaining portion is not removed by this kind of treatment and is presumably associated with portions of the junction remote from the edges of the cell.

Significant (approximately 6%) increases in output current at load point are attainable with printed aluminum back contacts despite the reduction in shunt resistance provided suitable firing conditions are obtained for achieving the P+ back field effect. All of the factors which are determinative with respect to firing conditions have not yet been identified.

Aluminum has been identified as an undesirable constituent in silver front metallization paste.

X-ray topographic studies of silicon under and adjacent to screen printed and fired patterns of candidate material for diffusion masking, aluminum back metallization and front metallization collector grids has shown that the composite structures can be processed through the necessary thermal cycles for cell fabrication without structural damage to the silicon.

Simple stress analysis suggests that the minimum glue line thickness may be limited by thermal stresses to values of the order of .008 or .009 inches for silicon solar cells having lateral dimensions of 4-5 inches bonded to glass with RTV silicone.

5.0 RECOMMENDATIONS

There are no recommendations to report.

6.0 CURRENT PROBLEMS

Delays caused by illness, a move into new facilities and technical problems have delayed parts of the program and slowed down the expenditure rate. In order to accommodate this departure from plan, a contract extension has been requested.

Our cell processing experiments have been infected by contaminant or other mechanism causing low shunt resistance. This problem precludes any useful development work on diffusion masking and causes some interference with other cell processing investigations. An intensive effort is underway to identify and eliminate the cause of the problem.

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