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"HIGH RESOLUTION, LOW COST SOLAR CELL CONTACT DEVELOPMENT"

FINAL REPORT

Contract 955725
CLPL-5

Prepared for:

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The JPL Low-Cost 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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1.0 SUMMARY STATEMENT

MIDFILM cell fabrication and encapsulation have been demonstrated as a means of applying low-cost solar cell collector metallization. The average cell efficiency of 12.0% (AM1, 28°C) was achieved with fritted silver metallization with a demonstration run of 500 starting wafers. A 98% mechanical yield and 80% electrical yield were achieved through the MIDFILM process. High series resistance was responsible for over 90% of the electrical failures and was the major factor causing the low average cell efficiency. Environmental evaluations suggest that the MIDFILM cells do not degrade. A slight degradation in power was experienced in the MIDFILM minimodules when the AMP Solarlok connector delaminated during environmental testing.

Molybdenum-tin-titanium hydride has been identified as a metallization for producing non-noble MIDFILM contacts. Efficiencies of 9 to 10% have been achieved for non-AR coated cells. The low efficiencies of the non-noble MIDFILM contacted cells is attributed totally to the series resistance associated with the grid line configuration.
2.0 INTRODUCTION

This Final Technical Progress Report covers the nine month period ending April 30, 1981. The scope of the contract covers the optimization, demonstration, and environmental evaluation of forming silver solar cell collector grid contacts by the MIDFILM process and the feasibility of forming grid contacts with non-noble metals. This is a proprietary process developed by Ferro Corporation, a subcontractor for the program. The cost effectiveness of the MIDFILM process for the collector grid contacts was found to be better than that of screen printing processes.

The MIDFILM process attains a line resolution comparable to photoresist methods with a process related to screen printing. The surface to be processed is first coated with a thin layer of photopolymer material. Upon exposure to ultraviolet light through a suitable mask, the polymer in the non-pattern area cross-links and becomes hard. The unexposed pattern areas remain tacky. The conductor material is applied in the form of a dry mixture of metal and frit particles which adhere to the tacky pattern area. The assembly is then fired to ash the photopolymer and sinter the fritted conductor powder.

The contract effort was divided into six tasks. Task I was to optimize the MIDFILM process parameters with a silver and frit metallization on solar cells processed by a baseline cell processing sequence shown in Figure 2.1-A. This optimized process was then to be demonstrated by fabricating 500 wafers into cells. Task II was to develop an interconnect technique and fabricate four (4 cell x 6 cell) minimodules from cells fabricated in the demonstration run. Some cells and two minimodules were then subjected to environmental test in Task III. Task IV explored the feasibility of forming MIDFILM collector grid contacts with non-noble metals. Task V required the preparation of process
specifications and procedures which would enable execution of the process by other companies. Task VI was to compile the necessary information, in the form of SAMICS Format A, to enable an economic evaluation of the process in comparison with other processes for applying collector contact metallization.
Figure 2.1-A

MIDFILM PROCESS SEQUENCE

SURFACE PREPARATION
30% NaOH

JUNCTION FORMATION
SPIN-ON DIFF SOURCE

P+ BACK
PRINT & FIRE Al

CLEAN Al BACK
HF + BRUSH CLEAN

SPIN-ON RESIN

EXPOSE RESIN

APPLY SILVER

FIRE CONTACT

JUNCTION CLEAN
LASER SCRIBE

TEST

AR COAT

TEST
3.0 TECHNICAL DISCUSSION

3.1 OPTIMIZATION OF PROCESS PARAMETERS

The optimization of the MIDFILM process parameters includes the selection of proper resin composition, optimum silver powder application technique, and composition and correct sintering conditions. The grid pattern design was developed assuming a minimum 50 μm line resolution with sintered silver-grid powder resistivity of $4.77 \times 10^{-6}$ Ω-cm and grid line height of 8.5 μm. Figure 3.1-A shows the grid line pattern used to fabricate 2.1 x 2.1 inch cells with a 39 mΩ calculated series resistance. The series resistance equations and calculations are given in Appendix 1.

Early in the contract the resin composition was changed to facilitate in meeting environmental OSHA requirements. The resin RW 3190 was evaluated using a process sequence similar to that of Figure 2.1-A. This RW 3190 resin appeared to be humidity sensitive, the resin dewetted the silicon after a few hours. Ferro modified the resin to produce RG 4933, which assures a 10-hour shelf life when dried wafers were stored prior to UV exposure.

During the previous contract it was determined that a spherical shaped silver powder gave the best packing density and lowest grid resistivity. The frit composition used to manufacture Thick Film Systems (TFS) 3347 silver paste was used in the MIDFILM powders. Powder compositions containing 2, 5 and 10% frit were procured from TFS and evaluated by the fabrication of cells. The evaluation of these compositions indicated that the 2% composition had a higher series resistance than the 5 or 10% composition. The 5% 3347 frit, 95% spherical shaped silver powder was selected for further evaluation in order to maximize metal content in the grid contacts. Ferro Corp. also
DIMENSIONS ARE IN INCHES
TOLERANCES: XXX = ± .003
PART NO. 6325-01

Figure 3.1-A
evaluated three silver powder compositions containing 2, 5 and 7% frit and one composition containing 3% frit and 2% silver fluoride. Table 3.1-A is a summary of this evaluation and comes to the same conclusion, that the 5% frit-silver powder is optimum.

Cells fabricated using this 5% frit composition and a 300°C dry step with a single 675°C sintering step, passed a tape pull test using 600 type Scotch tape. When solder coated interconnects were soldered to the contacts, the interconnections pulled at very low force. The surface of the silicon under the soldered area had a blue tint. This blue tint was probably due to the incomplete burn-off of the resin on the cells surface under the silver contacts.

Ferro recommended a 575°C pre-sintering step to allow the organics from the resins to be exposed to the oxygen atmosphere through the porous powder before sintering the contact into the continuous layer. An experiment was run to evaluate the pre-sintering step. This experiment indicated that a pre-firing step of 675°C at 36°/min belt speed (30 sec) to be optimum. The best cell of the group is shown in Figure 3.1-B and had a measured series resistance of 31 mΩ, which is lower than the theoretically calculated series resistance of 39 mΩ. The gridline thickness appears to be higher than previously assumed and was in agreement with Ferro's measurement of gridline thickness.

The solderability of contacts formed by the new firing procedure was evaluated under varying temperatures (340, 370 and 400°C) for 1 sec. The 45° pull strength of interconnection is listed in Table 3.1-B. The 370°C soldering for 1 sec. appeared to be optimum, with a minimum pull strength of 550 grams. During the previous contract, No. 955298, the pull strength of the ultrasonic back aluminum contact exceeded 1000 grams.
Table 3.1-A
COMPOSITIONS AND RESULTS FOR SEVERAL SILVER POWDERS

<table>
<thead>
<tr>
<th>Composition (Percent)</th>
<th>RH 3646-A</th>
<th>RH 3646-B</th>
<th>RH 3655</th>
<th>RH 3649-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFS Spherical Silver Powder</td>
<td>97</td>
<td>95</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>TFS No. 3347 Frit</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Silver Fluoride (AgF)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

Samples (640☐ Test Pattern on Etched Silicon Wafers)

<table>
<thead>
<tr>
<th>Resin Wgt. (milligrams/in²)</th>
<th>(1) 3.7</th>
<th>6.4</th>
<th>6.5</th>
<th>5.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) 5.5</td>
<td>5.4</td>
<td>5.9</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

Silver Powder (milligrams)

<table>
<thead>
<tr>
<th>(1) 24.5</th>
<th>32.3</th>
<th>35.9</th>
<th>33.5</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) 31.1</td>
<td>37.0</td>
<td>32.5</td>
<td>36.7</td>
<td></td>
</tr>
</tbody>
</table>

Fired Results (1 min., 675°C Box Furnace)

<table>
<thead>
<tr>
<th>Avg. Thickness (microns)</th>
<th>(1) 9.5</th>
<th>14.5</th>
<th>-</th>
<th>13.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) 13.5</td>
<td>16.2</td>
<td>16.1</td>
<td>15.3</td>
<td></td>
</tr>
</tbody>
</table>

Resistance (☐ for 640☐)

<table>
<thead>
<tr>
<th>(1) 2.86</th>
<th>2.09</th>
<th>2.26</th>
<th>2.13</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) 2.31</td>
<td>2.02</td>
<td>2.60</td>
<td>1.66</td>
<td></td>
</tr>
</tbody>
</table>

Sheet Resistance (milli☐/☐)

<table>
<thead>
<tr>
<th>(1) 1.7</th>
<th>1.9</th>
<th>-</th>
<th>1.8</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) 1.9</td>
<td>2.0</td>
<td>2.53</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

Scotch Tape Adherence

| Pass                                  | Pass      | Pass     | Pass     |           |

Scape-off

| Fair                                  | Good      | Good     | Fair-Good | Good      |

Solder Wetting (Alpha #611)

| Good                                  | Good      | Fair-Good| Good      |           |

Pull Strength

| 2                                     | 1         | 1        | 2         |           |

Bond Failure

| Ag/Si                                 | Si        | Si       | Ag/Si     |           |

---

1* Pass indicates no removal of Ag.

2* Fair-Good indicates metallization removed by scraping with razor blade—more force required for good rating.

3* 1 more force required than 2.

4* Ag/Si—interface between metallization and silicon wafer. Si—interface with chips of silicon pulled-out.
Figure J.1-B

36"/min Prefire
Series Resistance 31 MΩ

No AR Coating
Table 3.1-B

Soldering Results
45° Pull Test*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average Pull Strength</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 sec, 340°C</td>
<td>283 grams</td>
<td>One cell tab had no strength</td>
</tr>
<tr>
<td>1 sec, 370°C</td>
<td>643 grams</td>
<td>All cells at least 550 grams</td>
</tr>
<tr>
<td>1 sec, 400°C</td>
<td>531 grams</td>
<td>All cells at least 375 grams</td>
</tr>
</tbody>
</table>

5 cells were tested in each group.

*Pull Tab - 2 mil x 0.1 inch OFHC Copper Ribbon with Fused 0.5 mil Solder Plate
Observations of the wafer's surface between grids showed traces of silver particles. The residual traces of silver were due to incomplete removal of silver powder prior to firing. It was assumed that the exposed resin between grid lines was too soft and allowed the silver powder to become imbedded in the resin. A two step UV exposure experiment was evaluated to determine if the powder could be applied and a majority of the powder between grid lines could be removed without silver imbedment, followed by exposure of the total surface to UV a second time to harden the resin before final powder removal. It was concluded that the second exposure was unnecessary and the single exposure was optimum. Qualitatively it was found that the silver was more difficult to remove from the double exposed wafers.

Once these optimum parameters were established a lot of 25 cells was fabricated (Table 3.1-C) which had an average efficiency of 9.66% (13% with AR coating) and about a 60 mΩ series resistance, Figure 3.1-C.
Table 3.1-C

24" Per Minute, No AR Coating

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Voc</th>
<th>Isc</th>
<th>I_{500}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>596</td>
<td>639</td>
<td>559</td>
</tr>
<tr>
<td>22</td>
<td>596</td>
<td>628</td>
<td>534</td>
</tr>
<tr>
<td>21</td>
<td>593</td>
<td>621</td>
<td>545</td>
</tr>
<tr>
<td>36</td>
<td>597</td>
<td>642</td>
<td>574</td>
</tr>
<tr>
<td>24</td>
<td>595</td>
<td>626</td>
<td>543</td>
</tr>
<tr>
<td>13</td>
<td>594</td>
<td>633</td>
<td>553</td>
</tr>
<tr>
<td>23</td>
<td>596</td>
<td>615</td>
<td>528</td>
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<td>14</td>
<td>594</td>
<td>610</td>
<td>525</td>
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<td>17</td>
<td>596</td>
<td>623</td>
<td>552</td>
</tr>
<tr>
<td>15</td>
<td>596</td>
<td>639</td>
<td>567</td>
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<td>16</td>
<td>598</td>
<td>647</td>
<td>581</td>
</tr>
<tr>
<td>19</td>
<td>597</td>
<td>633</td>
<td>547</td>
</tr>
<tr>
<td>27</td>
<td>597</td>
<td>644</td>
<td>552</td>
</tr>
<tr>
<td>20</td>
<td>595</td>
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<td>541</td>
</tr>
<tr>
<td>34</td>
<td>596</td>
<td>625</td>
<td>563</td>
</tr>
<tr>
<td>18</td>
<td>595</td>
<td>640</td>
<td>472</td>
</tr>
<tr>
<td>33</td>
<td>599</td>
<td>661</td>
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<td>26</td>
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<td>35</td>
<td>600</td>
<td>661</td>
<td>570</td>
</tr>
<tr>
<td>28</td>
<td>598</td>
<td>660</td>
<td>581</td>
</tr>
</tbody>
</table>

Average: 596

Standard Deviation: 1.7

# of Cells Surviving

Laser Scribe: 23
3.2 PRODUCTION RUN OF OPTIMIZED PROCESS

A small production run of a process is necessary in order to identify problems by statistical methods. A 500 wafer start was selected as a reasonable number of cells for reliable data. This 500 wafer start was broken into 6 lots, 4 of 100 wafer starts and 2 of 50 wafer starts. The open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and current at 500 mV ($I_{500}$) was monitored for statistical distribution.

Table 3.2-A is the statistical distribution of $V_{oc}$, $I_{sc}$, and $I_{500}$ for the first 100 wafer lot. There was an 80% mechanical yield and a 58% electrical yield of 12.25% average efficiency at ANL. (Cells with less than a 9.8% efficiency are considered to be an electrical failure.) The $V_{oc}$ population is skewed to lower voltages, indicating a possible fabrication problem resulting in a biased distribution. The moments of the $I_{sc}$ and $I_{500}$ definitely indicated a bimodal distribution of two different populations, the better distribution (cells with $I_{500}$ above 620 ma, 10.9% efficiency) with an average efficiency of 12.67%, and the lower distribution with an average efficiency of 10.2%. In reviewing the other fabrication lots, Tables 3.2-B, C, D and E, the distribution of the $I_{500}$ appears to be bimodal or very broad.

In reviewing the distribution of the entire production run, Table 3.2-F, the $I_{sc}$ and $I_{500}$ cell distribution appears bimodal. The low yield of the total production was due to diffusion source problems occurring during the drying of the PX-10 source. The poor drying cycle for the PX-10 diffusion source resulted in the rejection of 170 wafers due to poor probe voltage after the $P^+$ back contact was applied. Approximately 60 wafers or 18% of the remaining 330 wafers were broken during the processing. During the application of the MIDFILM contact the mechanical loss was approximately 2%.

-14-
Table 3.2-A
Table 3.2-B

-16-
Table 3.2-D
Table 3.2-F

-20-
Approximately 20% of the 268 finished cells were electrical failures (cells with less than a 9.8% efficiency). These electrical failures are primarily due to high series resistance. A number of cells from Run 1-13-8.1 were silver plated in a cyanide solution to increase the grid line thickness by 6μ and bridge gaps on discontinuous grid lines. Table 3.2-G is the histogram of current at 500 mv of cells before and after plating. All cells which were plated (initially electrical failures) were increased above 9.8% efficiency. Figure 3.2-A is the I-V characteristic curves of the same cell without an AR coating before and after plating. The curve fill factor (CFF) increased from .504 to .726 due to the reduction of series resistance. It must be noted that the plating solution used to plate these cells attacked the frit in the paste and caused peeling of the contact after a tape pull test.

From this small production run of MIDFILM contacted cells, it can be concluded that:

1. The mechanical loss due to handling can be maintained at approximately 2%,

2. The major electrical yield problem is due to series resistance,

3. Electrical yield can be raised from 80% to 99% with a plating process or comparable process to bridge gaps in discontinuous grid lines, and

4. The efficiency will be better than 12% AM1.
Before Plating

$I_{500} (657.0 \pm 9.8) \text{ mA}$

*Average of good cells

After Plating

$I_{500} (657.1 \pm 55.5) \text{ mA}$

*Average of good cells

Table 3.2-G
Figure 3.2-A

EFFECT OF SILVER PLATING ON POOR MIDFILM CELL

Before Plating
CFF = 0.504

After Plating
CFF = 0.726
Cells fabricated in the 500 cell production run were used in the fabrication of the minimodules. These glass superstrate mini-modules were fabricated using a double vacuum bag lamination technique with ethylene vinyl acetate (EVA) as the pottant.

The EVA formulations used in fabrication of the modules has been prepared by Springborn Laboratories (Enfield, CT). The clear No. A-9918 is based on Elvax 150 EVA with cross linking agents, UV screening compounds and anti-oxidants. The final product is an extruded sheet ~16 mils thick. More detailed formulation may be obtained by contacting Springborn Laboratories.

These formulations are well suited to the solar cell encapsulation application. When heated, the material passes through a thermoplastic stage at which time gas removal is easily achieved. At a higher temperature the peroxides in the formulation decompose and cause thermosetting through cross-linking of the saturated backbone of the polymer.

The double vacuum bag laminating technique was developed under a previous contract. The design of the fixture utilized in this technique is shown in Figure 3.3-A. An oven was used as a heat source in place of the silicon heater.

The lamination procedure commences by placing the module in the bottom vacuum bag chamber. A 0.010 Teflon FEP sheet is used as a release sheet. A 1/8" silicone face sheet over the Teflon completes this chamber. Nylon sheeting is used as the vacuum bagging material. The second chamber contains a 1/8" aluminum sheet and scrim cloth to ensure easy evacuation. A laminating sequence consists of first evacuating both chambers and heating the module, then releasing the top vacuum and heating.

(1) DOE/JPL 954853-80/9 (Task IV)
LAMINATING FIXTURE

Figure 3.3-A

AG 7/24/80
Figure 3.3-B shows the thermal cycle used during lamination. Initially the module sees the pressure through the 1/8" aluminum sheet. This sheet effectively bridges the pressure across the intercell spaces which allows gases to migrate to the edges and be removed. The 1/8" silicone sheet cushions any high points on the cells which might lead to breakage. After a suitable time period, atmospheric pressure is allowed to enter the top compartment. Pressure is now felt by the module through the silicone and Teflon sheets only; thus the EVA is molded into the intercell spaces as well as to the cell backs. Thermosetting of the EVA is complete in this mode when more heat is applied.

Four minimodules were laminated by the double vacuum bag technique discussed above. The following list represents the recommended layup order of materials:

a) 1/8" soda lime window glass  
b) 5 mil Crane-Glas 230  
c) Clear EVA  
d) Cell circuit  
e) 5 mil Crane-Glas 230  
f) White EVA  
g) 5 mil Crane-Glas 230  
h) 1 mil Al/Polyester film

There was no evidence of transmittance loss by utilizing a 5 mil Crane-Glas in front of the cells. The lamination cycle was 28 minutes long with release of the upper vacuum bag vacuum when the module temperature reached 105°C. Work done on another JPL contract (2) has indicated that the use of Crane-Glas in front of the cells leads to less than 1% transmittance loss. Figures 3.3-C, D, E and F show the I-V curves under an AM1 pulsed solar simulator for the four minimodules constructed. There was approximately a 13% loss with the use of the soda lime window glass and a 5% loss due to cell mismatch.

(2) DOE/JPL 995567 (Task III)
Figure 3.3-B

TIME/TEMPERATURE/PRESSURE CYCLE - SOLAR MODULES (Double Vacuum Bag Technique)

1. Assemble module, load into double vacuum bag.
2. Evacuate both cavities for 20 minutes, start heating.
3. Release top cavity vacuum at 100°C point.
4. Raise temperature to 150°C.
5. Cool, remove module.
Figure 3.3-C
Figure 3.3-C

SOLAR CONVERTER E I CURVE

SPECTROLAB QC FORM 3001
SYLMAR, CALIFORNIA DATE: 4/28/81

PROJECT:

SERIAL NO. MIDFILM #2

☐ CELL ☐ MODULE ☐ PANEL DESIGNATION:

☐ AM1

SOURCE: ☐ SUN ☐ TUNGSTEN ☐ XENON

☐ COLLIMATED ☐ UNCOLLIMATED

TEST TEMP.: 28 °C 82 °F

TEST NO. PROC. NO.

Isc = Voc = Pmp =

By: [Signature]
Figure 3.3-E
Figure 3.3-F
The modules were completed using AMP Solarlok connector bonded to the backside with an epoxy adhesive. The panels were then mounted in an extended aluminum frame using a 1/16" neoprene gasket.
3.4 ALTERNATE MATERIALS

As part of Spectrolab's effort to reduce the cost of terrestrial cell manufacturing, a task was established with Ferro Corp. to investigate the usage of alternative materials. During this contract copper, nickel, tungsten-tin and molybdenum-tin compositions were investigated as possible alternative materials. Silver plated copper particles were also investigated as a possible alternative material.

The investigation into air-fired copper and nickel compositions supplied by TFS proved futile. The evaluation performed by Ferro is summarized in Table 3.4-A and indicates that nickel has a very poor conductivity, adherence and solderability. The copper composition had a poor solderability also.

Tin based alloys were selected as the next powder to be investigated. They included tungsten, nickel and molybdenum-tin powders; exact compositions are given in Table 3.4-B. The nickel and molybdenum powders with 15% tin and the tungsten powder with 80% tin had very poor adherence. The molybdenum and molybdenum oxide powders with 80% tin and 0.5% titanium hydride had good adherence and a variable resistivity (5.5 to $\infty$ Ω for the 640□ pattern). Cells were fabricated using the A, B, C and D molybdenum-tin compositions, pre-heated at 400 to 500°C for 30 min. in air, and fired at 675°C once or twice for 36 min. in 95% N₂ and 5% H₂ atmosphere. Figure 3.4-A is a composite I-V characteristic of 12 cells heat treated and fired under conditions shown in Table 3.4-C. The shunt resistance of these cells are also shown in Table 3.4-C and indicate that the cells manufactured with TiH₂ have excellent shunt resistance. The major problem with all of these powders is the high resistance of the sintered powders, which results in a high series resistance for the cells.
Table 3.4-A

RESULTS FOR TFS AIR-FIRING COPPER (#5514) AND NICKEL (#5517)

<table>
<thead>
<tr>
<th>Samples (640 test pattern on etched silicon wafers)</th>
<th>Copper (#5514)</th>
<th>Nickel (#5517)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Wgt. (milligrams/in²)</td>
<td>(1) 6.3</td>
<td>(1) 5.8</td>
</tr>
<tr>
<td></td>
<td>(2) 6.3</td>
<td></td>
</tr>
<tr>
<td>Power Wgt. (milligrams)</td>
<td>(1) 20.8</td>
<td>(1) 17.2</td>
</tr>
<tr>
<td></td>
<td>(2) 19.4</td>
<td>(2) 15.6</td>
</tr>
</tbody>
</table>

Fired Results (1 min., 675°C Box Furnace)

| Resistance (Ω for 640 )                            | (1) 15.4   | (1) 85.9     |
|                                                   | (2) 15.9   | (2) 101.5    |
| Scotch Tape Adherence¹*                            | Pass       | Fail         |
| Scrape-off²*                                       | Excellent  | Poor         |
| Solder Wetting³*                                    | None       | None         |
| Appearance of Metallization at 45X Magnification   | Mud-cracking and Blistered | Cracks Along Edges |

¹* Pass indicates no removal of metal
   Fail indicates some metal removal

²* Scraping with razor blade

³* 63 Sn/37 Pb solder; Alpha #611 and Blackstone #642 solder fluxes

⁴* Nickel samples showed a trace of discoloration on substrate at edge of metallization.
### Table 3.4-B

**Composition and Results for Alternate Materials**

<table>
<thead>
<tr>
<th>Composition (Percent)</th>
<th>A CN 3659-B</th>
<th>B CN 3659-C</th>
<th>C CN 3659-D</th>
<th>D CN 3665</th>
<th>E CN 3662</th>
<th>F CN 3659-A</th>
<th>G CN 3659-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holmium (Sylvania 280-325)</td>
<td>20</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Polychromic Oxide (Reagent)</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>19.5</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tungsten (Sylvania H-20)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel (Inco 123)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tin (Atlantic Equipment Engineers 59366)</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>Titanium Hydride (Perino Plant PK-41)</td>
<td>80</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Fired Results**

- **Color of Metallization After Preheat**
  - a. 30 min. 400°C (air)
  - b. 30 min. 500°C (air)
  - c. one min. 675°C (air)

- **Appearance of Metallization After Firing at 675°C-25/min. (92% H2, 5% H2)**
  - a. silver
  - b. dark brown
  - c. silver brown coat

- **Total Firing Time - 36 minutes**
  - a. silver
  - b. silver
  - c. silver brown coat

- **Time at Peak - Approx. 5 minutes**
  - a. silver
  - b. silver brown coat

- **Resistance (Average 640Ω)**
  - a. 30.67
  - b. 10.7
  - c. 12.5

- **Scotch Tape Adherence**
  - a. pass
  - b. pass
  - c. pass

- **Scratches Resistance**
  - a. good
  - b. good
  - c. fair

- **Soldier Wetting (Spectrolab leads, alpha 611 flux)**
  - a. fair

- **Pull Strength**
  - a. similar to silver

_GMJ/jmg_
_d/13/81_
Figure 3.4-A
<table>
<thead>
<tr>
<th>Cell #</th>
<th>Powder Composition</th>
<th>30 min. Preheat Condition</th>
<th># of 36 min. Firings</th>
<th>R&lt;sub&gt;sh&lt;/sub&gt;(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>RH 3659-C(A)</td>
<td>400</td>
<td>1</td>
<td>260</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>500</td>
<td>1</td>
<td>310</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>500</td>
<td>2</td>
<td>116</td>
</tr>
<tr>
<td>1</td>
<td>RH 3659-C(B)</td>
<td>400</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>500</td>
<td>1</td>
<td>125</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>500</td>
<td>2</td>
<td>333</td>
</tr>
<tr>
<td>5</td>
<td>RH 3659-C(C)</td>
<td>400</td>
<td>1</td>
<td>333</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>500</td>
<td>1</td>
<td>116</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>500</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>RH 3665 (D)</td>
<td>400</td>
<td>1</td>
<td>310</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>500</td>
<td>1</td>
<td>750</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>500</td>
<td>2</td>
<td>500</td>
</tr>
</tbody>
</table>
To reduce the series resistance of the metallization, cell numbers 4 and 9 were electrically plated with 2-3 μm of silver in a cyanide solution and heat treated for 4 min. at 300 to 400°C in air. Figures 3.4-B and C show the change in I-V characteristics before and after plating. There was a marked increase in the metallization conduction after plating and after the heat treatment.

A second set of cells was fabricated using the tin compositions with titanium hydride in order to improve and verify the results of Figure 3.4-A. Compositions RH 3659-C(B) and RH 3665-D) were applied to eight wafers each and pre-heated to 500°C for 30 min. Four wafers of each composition were then sintered twice at 675°C for 36 min. in 95% N₂ and 5% H₂ atmosphere. The other four wafers of each composition were then sintered three times at the same temperature and atmosphere. The RH 3665(D) had sufficient series resistance to result in poor curve shape for both sintering conditions. The RH 3659-C(B) had a series resistance of about 110 mΩ (agreement with calculated series resistance, Appendix A), and a fair curve shape. The efficiency (η, without AR coating), curve fill factor (CFF) and shunt resistance (R_{shunt}) are given in Table 3.4-D for both sintering conditions. The efficiency and curve fill factor are similar for both sintering conditions but the shunt resistance appears slightly higher for the cells sintered three times. The efficiencies of the cells are from 9 to 10% without an AR coating which is extremely good for this highly resistive material. The particle size distribution curves for the tin and molybdenum powders used in RH 3659-C are given in Tables 3.4-E and 3.4-F respectively. The molybdenum is ideal for MIDFILM application but the tin is slightly coarse.

The prospects of silver plating copper powder was addressed as a possible alternative material. In Figure 3.4-D photomicrographs
Figure 3.4-B

I-V CHARACTERISTICS OF RH 3665
MIDFILM CELL BEFORE AND AFTER SILVER PLATING

Before Plating
\( \eta_{AR} = 7.6\% \)

After Plating
\( \eta_{AR} = 10.0\% \)
Figure 3.4-C

I-V CHARACTERISTIC OF RH 3659-C MIDFILM CELL
BEFORE AND AFTER SILVER PLATING

Before Plating
$R_s = 185 \, \text{m} \Omega$
$\eta_{AR} = 11.4\%$

After Plating
$R_s = 96 \, \text{m} \Omega$
$\eta_{AR} = 13.3\%$
CHARACTERISTICS OF Mo-Sn-TiH₂ POWDER

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>( \eta^* )</th>
<th>CFF</th>
<th>( R_{\text{shunt}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder RH3659-C, sintered two times at 675°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>9.84</td>
<td>.686</td>
<td>71.9</td>
</tr>
<tr>
<td>54</td>
<td>9.70</td>
<td>.705</td>
<td>202</td>
</tr>
<tr>
<td>57</td>
<td>9.71</td>
<td>.689</td>
<td>169</td>
</tr>
<tr>
<td>58</td>
<td>9.49</td>
<td>.684</td>
<td>211</td>
</tr>
<tr>
<td>Powder RH3659-C, sintered three times at 675°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>9.07</td>
<td>.650</td>
<td>301</td>
</tr>
<tr>
<td>55</td>
<td>9.66</td>
<td>.679</td>
<td>222</td>
</tr>
<tr>
<td>56</td>
<td>9.78</td>
<td>.699</td>
<td>342</td>
</tr>
<tr>
<td>87</td>
<td>9.46</td>
<td>.688</td>
<td>735</td>
</tr>
</tbody>
</table>

\*\( \eta \) = efficiency without AR coating
PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION
Tin Powder SN 266

Density 5.75 g/cc LIQUID
Preparation

Density 75 g/cc Viscosity 1.45 cp

DATE 9-7-79

BY G.P.

TEMPERATURE 33 °C
RATE 4.69 START DIA. 4.0 μm

Table 3.4-2
Tin Powder - Atlantic Equipment Engineer SN 266
1-5
In Figure 3.4-D photomicrographs (SEM-semographs) are shown for three copper powders investigated. Type A, Alcan MD-183, is an atomized-shot powder. It is composed of discrete particles, more or less spherical in shape, and has a low surface area. The particle size distribution curve, Figure 3.4-E, shows a range of sizes between about 4 to 50 microns with approximately 75% finer than 20 microns and 40% finer than 10 microns. This powder is somewhat coarse for good MIDFILM application or thick film inks. Although large particles are now shown in the photograph (chosen to show the character of the particle), the two methods for determining size distribution agree quite well because of the low degree of agglomeration in this kind of powder.

Precipitated copper powder, as typified by Metz No. 1 - B in Figure 3.4-D, is characterized by very fine particles highly agglomerated or aggregated. It is thought that the distribution curve shown in Figure 3.4-F shows predominantly the size of aggregates rather than agglomerates since ultrasonic dispersion shifts the curve only a small amount. This type of powder is suitable for MIDFILM and inks.

Ferro RZ4916 copper powder, Type C in Figure 3.4-D, is composed of amorphous particles, some of which are almost plate-like in character. The degree of agglomeration is low and the size distribution shown in Figure 3.4-G agrees quite well with that illustrated in the photograph. It can be used in thick film ink and is suitable for MIDFILM applications except for very fine lines (less than 2 mils wide). Attempts were made to coat this powder with silver.

The character of the Metz silvered copper powder No. 3 (Batch 8117) is shown in Figure 3.4-H, and the size distribution curve is given in Figure 3.4-I. It is extremely coarse and totally unsuitable for MIDFILM application. The particles appear to be
Figure 3.4-D
THREE TYPES OF COPPER POWDER
A. ALCAN 183 (Atomized)
B. METZ No. 1 (Precipitated)
C. FERRO RZ4916
PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION  183 - Copper - Lot 4756
Density 9.92 g/cc  LIQUID A-12  Density 805 g/cc  Viscosity 3.483 cp
Preparation

DATE 10-1-80
BY Sara Freeman
TEMPERATURE 32 °C
RATE 961 START DIA. 70 μm

EQUIVALENT SPHERICAL DIAMETER, μm

Figure 3.4-E
MICROANALYSIS OF COPPER
Figure 3.4-F
METZ NO. 1 COPPER
PARTICLE SIZE DISTRIBUTION

DATE 8-25-80
BY SOCA FREEMAN
TEMPERATURE 34°C
RATE 744 START DIA 60 µm

PARTICLE SIZE DISTRIBUTION

METZ Cu #1 W.T. 10121
Density 8.92 g/cc Liquid A-10
Viscosity 3.328 cp

EQUIVALENT SPHERICAL DIAMETER, µm

PREPARED:
Figure 3.4-G
FERRO RZ4916 COPPER
PARTICLE SIZE DISTRIBUTION

DATE 2-3-81

BY Sara Freeman

TEMPERATURE 3.2°C

RATE 939 START DIA. 70 μm

SAMPLE IDENTIFICATION
Ferro RZ4916 Copper

DENSITY 8.92 g/cc

PREPARATION Liquid

VISCOSITY 3.592 cp

POROUS STERILIZATION
Figure 3.4-H
METZ NO. 3 SILVERED COPPER POWDER

ORIGINAL PAGE IS OF POOR QUALITY
Figure 3.4-I
METZ NO. 3 SILVERED COPPER
PARTICLE SIZE DISTRIBUTION

DATE: 6-8-81
BY: Sara Freeman

TEMPERATURE: 32 °C
RATE: 938
START DIA.: 70 μm

METZ Silvered Copper
Sample: 8117
Density: 8.92 g/cc
Liquid: 905 g/cc
Viscosity: 3.512 cp

EQUIVALENT SPHERICAL DIAMETER, μm

MICROMERITICS®
INSTRUMENT CORPORATION
aggregates, which could account for the very rough surface. Many of the aggregates are very large and settle so rapidly they are not recorded on the sedimentation curve. The cross section of a typical particle indicates that about 90% of the copper surface is coated with silver. Incomplete coating appeared to be associated with the deeper crevices in the particle. This powder is reported to contain 3% silver by weight and it appears to be evenly distributed over the copper particles in a layer about one micron thick. It is not a protective coating since the powder fired one minute in air at 675°C was black indicating the formation of copper oxide (CuO). Although nothing is known about the copper powder used by Metz as a starting material, or the procedure used in coating it, the cross section semographs suggest that the powder was coarse before coating. It does not appear that the particles are aggregates of smaller particles, each coated by silver, i.e., that the silver is the glue holding the aggregate together.

Attempts to silver coat RZ4916 copper powder by a proprietary electroless plating process were not successful. No coating has taken place and the powder is simply a mixture of copper particles and finely divided, precipitated silver.

Although the testing of the Ferro process was very limited, it does not appear to be a suitable procedure for coating fine copper powder having the size distribution desirable for MIDFILM application or thick film ink. The Metz process may be more feasible. If, as the micrographs indicate, they started with a coarse copper powder, it would be well to have them try coating a much finer powder - one in which the top size (individual particle or aggregate) is about 10 microns.

For use on silicon photovoltaic cells, it is necessary that the integrity of the silver coating on copper powder must be essentially 100%. No conclusion can be drawn from this work whether
or not such a powder having a proper size distribution can be prepared.

The results of the investigation into alternative materials indicate that a molybdenum-tin-titanium hydride metallization applied by the MIDFILM process and plated with a thin layer of silver or other conductive material is a good candidate for replacing silver powder in the manufacturing of low cost solar cells.
3.5 ENVIRONMENTAL TEST

The terrestrial environment can be one of the major contributions to the high cost of photovoltaic arrays. Premature environmental failure of panels or cells could dramatically increase cost by reducing array lifetime. Laboratory environmental testing can predict failure and identify causes for failure in a terrestrial environment.

To determine the terrestrial environmental survivability of the MIDFILM processed cells and minimodules, cells fabricated during the production run and laminated minimodules were subjected to humidity and thermal cycle tests. Fifteen (15) cells and one minimodule were subjected to humidity (90-95% RH, 40-45°C) test followed by thermal cycle (50 cycles - 40°C to 90°C) test. Fifteen (15) other cells and another minimodule were subjected to thermal cycle test and then humidity test. These tests were performed in accordance with JPL Specification 5-342-1C. There was less than a 1% change in I-V characteristics of the cells and the module that was subjected to thermal cycle test and then humidity test. The epoxy adhesive used to bond the AMP Solarlok connector to the module delaminated during the humidity test after the thermal cycle and allowed moisture to enter the module. This module showed no degradation after thermal cycle but degraded 6% after humidity. Figures 3.5-A and B show the I-V characteristic curves of the modules after environmental test.
Figure 3.5-A

SOLAR CONVERTER EI CURVE

SPECTROLAB

SYLMAR, CALIFORNIA

DATE: 8/8/81

PROJECT: MIDFILM #3

HUMIDITY FOLLOWED BY THERMAL CYCLE

CELL MODULE PANEL DESIGNATION:

AM1

SOURCE: XENON 

COLLIMATED 

TEST TEMP.: 28 °C 78 °F

TEST NO. PROC. NO.

ISC = Voc = PM =
Figure 3.5-B

SOLAR CONVERTER E I CURVE
SPECTROLAB 2 C FORM 3001
SYLHAR, CALIFORNIA DATE: 9/8/81

PROJECT: MIDFILM 4. Thermal Cycle followed by Humidity
SERIAL NO.

CELLOMODULE PANEL DESIGNATION:
AM1 PARA #8 557

SOURCE: SUN TUNGSTEN XENON
COLLIMATED UNC Collimated

TEST TEMP: 28 °C 82 °F
TEST NO. PROC. NO.

Pmp = Voc =

BY
The MIDFILM contact has been demonstrated to produce cells of efficiencies above 14% and average of 12% (AM1, 28°C) on runs of 500 starting wafers. Powder compositions similar to those of screen printed silver paste were shown to be suitable for MIDFILM metallization. A 98% mechanical yield associated with breakage and 80% electrical yield associated with high series resistance were achieved through the MIDFILM process. Series resistance remains the major contributing factor responsible for low efficiencies and yield. MIDFILM cells were shown not to degrade under environmental evaluation. The MIDFILM minimodules had a 6% power degradation when the AMP Solarlok connector delaminated during the thermal shock test followed by humidity test. The minimodule which had experienced a humidity test followed by thermal shock had not shown any degradation.

Molybdenum-tin-titanium hydride MIDFILM metallization has been shown to produce cells of 9-10% efficiencies without an AR coating. The low efficiency of the non-noble metal was totally attributed to the series resistance associated with the grid line configuration.
APPENDIX I

CALCULATION OF SERIES RESISTANCE
CALCULATION OF SERIES RESISTANCE

A) BASE MATERIAL RESISTANCE

\[ R_B = \text{resistance} \]
\[ \rho_{Si} = \text{resistivity of silicon} \]
\[ t = \text{thickness of wafer} \]
\[ A = \text{area of wafer} \]
\[ R_B = \frac{\rho_{Si} t}{A} \]  

B) RESISTANCE OF DIFFUSED SURFACE LAYER

\[ \rho_s = \text{surface resistivity} \]
\[ l_o = \text{length of grid line} \]
\[ (\text{assuming grid lines go to edge of} \]
\[ \text{wafer}) \]
\[ x_o = \text{half distance between grid lines} \]
\[ j = \text{current density}^* \]

The element of power loss over an element of silicon \( dx \), is the square of the current entering that element times the resistance of that element \( dx \).

\[ dp = (j l_o x)^2 \cdot (\rho_s \frac{dx}{l_o}) \]  
\[ dp = j l_o \rho_s x^2 dx \]

integrating over the half distance between grid lines \( x_o \) gives the total voltage drop to the midpoint.

*As a first approximation of power loss, the current density \( j \) is assumed to be independent of distance from gridline.
\[ \Delta p = j^2 \rho_s l_0 \int_0^{x_0} x^2 \, dx \]

\[ = \frac{1}{3} j^2 \rho_s l_0 x^3 \bigg|_0^{x_0} \]

\[ \Delta p = \frac{1}{3} j^2 \rho_s l_0 x^3 \]

(4)

The total resistance over the half distance between grid lines is:

\[ R = \frac{\Delta p}{j^2 \rho_s l_0 x^2} \]

(5)

\[ = \frac{\rho_s x_0}{3l_0} \]

(6)

These areas of half distance between grid lines are all in parallel.

\[ R_D \text{ (total)} = \frac{\rho_s x_0}{3l_0} + \text{number of areas} \]

(7)

C) RESISTANCE OF GRID LINES

\[ \rho_{AG} = \text{resistivity of silver paste} \]

\[ l_0 = \text{length of grid lines (assuming grid lines go to end of wafer)} \]

\[ w_m = \text{minimum width of grid line} \]

\[ w_n = \text{maximum width of grid line} \]

\[ x_0 = \text{half distance between grid lines} \]

\[ j = \text{current density} \]
Considering one half the grid line, the element of power loss over an element of grid line \( dl \), is the square of the current entering that element times the resistance of that element \( dl \).

\[
dp = (x_o j l)^2 \cdot \left( \frac{\rho_{Ag} dl}{WH} \right) \quad (8)
\]

\[
dp = \frac{j^2 \rho_{Ag} x_o^2 l^2 dl}{WH} \quad (9)
\]

\( w \) can be expressed as

\[
w = \frac{1 (w_n - w_m) + l_ow_m}{2 l_o}
\]

Integrating over the whole grid line, and taking each side of the grid as two resistors in parallel:

\[
P = \frac{4 l_o x_o^2 j^2 \rho_{Ag}}{H} \int_0^{l_o} \left[ \frac{1^2 dl}{l_ow_m + 1(w_n - w_m)} \right]
\]

Form of

\[
\int x^2 dx = \frac{x^2}{a + bx} = \frac{x^2}{2b} - \frac{ax}{b^2} + \frac{a^2}{b^3} \ln (a + bx)
\]

(except where \( b \) approaches 0.)

\[
P = 4 \left( \frac{j^2 x_o^2}{H(w_n - w_m)} \right) \frac{1^0 \rho_{Ag}}{l_o} \left[ \frac{1/2}{w_n - w_m} + \frac{w_m}{w_n - w_m} \right] \ln \left( \frac{w_n}{w_m} \right)
\]

(except where \( w_n \approx w_m \))

Then the resistance over the whole grid line becomes:

\[
R = \frac{\Delta P}{4j^2 l_o x_o^2}
\]
\[ R_G (\text{Total}) = R/v \]

\( v = \text{number of grid lines} \)

\[
R_G (\text{Total}) = \frac{1_{o_{Ag}}}{vH(w_n-w_m)} \left[ \frac{1}{2} \left( \frac{w_m}{w_n-w_m} \right) + \left( \frac{w_m}{w_n-w_m} \right)^2 \right] w_n \frac{1}{w_m}
\]

(Except where \( w_n \neq w_m \))
D) OHMIC COLLECTOR

\( \rho_{Ag} \) = resistivity of silver paste

\( l_o \) = average distance between ohmic and edge of cell

\( w_i \) = minimum width of ohmic collector

\( w_f \) = maximum width of ohmic collector

\( L_o \) = length of ohmic collector

\( j \) = current density

Considering one half the cell, the element of powder loss over an element of ohmic collector \( dl \), is the square of the current entering that element times the resistance of the element \( dl \).

\[
dP = (l_o j)^2 \cdot \frac{\rho_{Ag} \, dl}{w_o^2} \quad (13)
\]

\( w_i \) can be expressed as

\[
w_i = \frac{j (w_f - w_i) + L_o \, w_i}{2 \, L_o} \quad (14)
\]

Integrating over the whole ohmic

\[
P = \frac{4 \, L_o}{H_o} \, l_o^2 \, j^2 \, \rho_{Ag} \int_0^{L_o} \left[ \frac{l^2 \, dl}{L_o \, w_i + l (w_f - w_i)} \right] \quad (15)
\]
Form of:

\[ \int_{0}^{C} \frac{x^2}{a + bx} \, dx = \frac{x^2}{2b} - \frac{a x}{b^2} + \frac{a^2}{b^3} \ln (a + bx) \]  

(16)

(except where \( b \) approaches \( 0 \))

\[ P = \frac{4 (j^2 L_0^2 L_o^2)}{H_o (w_f - w_i)} \left[ \frac{1}{2} \left( \frac{w_i}{w_f - w_i} \right) + \left( \frac{w_i}{w_f - w_i} \right)^2 \ln \frac{w_f}{w_i} \right] \]  

(17)

(except where \( w_f \approx w_i \))

Then the resistance over the whole cell becomes:

\[ R = \frac{\Delta P}{4 j^2 L_0^2 L_o^2} \]

\[ R_o \ (Total) = \frac{\Delta P}{4 j^2 L_0^2 L_o^2} = \frac{L_o \rho_{Ag}}{H_o (w_f - w_i)} \left[ \frac{1}{2} \left( \frac{w_i}{w_f - w_i} \right) + \left( \frac{w_i}{w_f - w_i} \right)^2 \ln \frac{w_f}{w_i} \right] \]  

(18)

(except where \( w_f \approx w_i \))
SAMPLE CALCULATION OF SERIES RESISTANCE
FOR GRID PATTERN #6325-01, FIGURE 3.1-A
SILVER POWDER #RH 3646-B

\[ \rho_{si} = 3.0 \ \Omega \cdot \text{cm} \]
\[ t = 0.033 \ \text{cm} \]
\[ A = 28.45 \ \text{cm}^2 \]
\[ \rho_s = 35 \ \Omega/\square \]
\[ l_o = 2.54 \ \text{cm} \]
\[ X_o = 0.104 \ \text{cm} \]
\[ \rho_{Ag} = 4.77 \times 10^{-6} \ \Omega \cdot \text{cm} \]
\[ W_m = 0.005 \ \text{cm} \]
\[ W_n = 0.01 \ \text{cm} \]
\[ H = 0.85 \times 10^{-3} \ \text{cm} \]
\[ W_i = 0.152 \ \text{cm} \]
\[ W_f = 0.610 \ \text{cm} \]
\[ H_o = 0.85 \times 10^{-3} \ \text{cm} \]
\[ L_o = 5.18 \ \text{cm} \]

Number of gridlines = 52

A) Base Material Resistance

\[ R_B = \frac{\rho_{si} t}{A} = \frac{(3.0)(0.033)}{28.45} \ \Omega = 3.48 \ \text{m}\Omega \]

B) Resistance of Diffused Surface Layer

\[ R_o = \frac{\rho_s X_o}{3 \cdot 104} = \frac{(35)(0.104)}{3(2.54)} \ \Omega \div 104 = 4.59 \ \text{m}\Omega \]
C) Resistance of Gridlines

\[
R_G = \frac{\rho_{Ag}}{H} \frac{L_o}{(w_n - w_m)} \left[ \frac{1}{2} \left( \frac{w_m}{w_n - w_m} \right) + \left( \frac{w_m}{w_n - w_m} \right)^2 \ln \frac{w_n}{w_m} \right] \div 52
\]

where \( w_n \neq w_m \)

\[
-\frac{(4.77 \times 10^{-6})(2.54)\Omega}{(.85 \times 10^{-3})(.005)} \left[ \frac{1}{2} \left( 1 + \ln 2 \right) \right] = 10.59 \text{ m\Omega}
\]

D) Resistance of ohmic collector

\[
R_o = \frac{\rho_{Ag}}{H} \frac{L_o}{(w_f - w_i)} \left[ \frac{1}{2} \left( \frac{w_i}{w_f - w_i} \right) + \left( \frac{w_i}{w_f - w_i} \right)^2 \ln \frac{w_f}{w_i} \right]
\]

where \( w_f \neq w_i \)

\[
-\frac{(4.77 \times 10^{-6})(5.18)}{(.85 \times 10^{-3})(.458)} \left[ \frac{1}{2} \left( \frac{.152}{.458} \right) + \left( \frac{.152}{.458} \right)^2 \ln \frac{.610}{.152} \right]
\]

\( R_o = 20.38 \text{ m\Omega} \)

Total resistance of contact pattern is:

\( 3.48 + 4.59 + 10.59 + 20.38 = 39.04 \text{ m\Omega} \)
SAMPLE CALCULATION OF SERIES RESISTANCE FOR GRID PATTERN #6325-01, FIGURE 3.1-A
Mo-Sn-TiH₂ POWDER #RH 3659-C

ρ₀₄ = 3.0 Ω·cm

ρ₀₅ = 35 Ω/□

ρ₀₆ = 0.033 cm

A = 28.45 cm²

l₀ = 2.54 cm

X₀ = 0.104 cm

ρ₀₇ = 29.5 x 10⁻⁶ Ω·cm

Wₘ = 0.005 cm

Wₙ = 0.01 cm

H = 1.5 x 10⁻³ cm

Wₗ = 0.152 cm

Wₙ = 0.610 cm

H₀ = 1.5 x 10⁻³ cm

L₀ = 5.18 cm

Number of gridlines = 52

A) Base Material Resistance

Rₐ = \frac{ρ₀₄ t}{A} = \frac{(3.0) (0.033)}{28.45} Ω = 3.48 mΩ

B) Resistance of Diffused Surface Layer

Rₒ = \frac{ρ₀₅ X₀}{3 l} ÷ 104 = \frac{(35) (0.104)}{3(2.54)} Ω ÷ 104 = 4.59 mΩ
C) Resistance of Gridlines

\[ R_G = \frac{\rho_{\text{Mo-Sn}}}{H} \left( \frac{1}{2} \left( \frac{w_m}{w_n - w_m} \right) + \left( \frac{w_m}{w_n - w_m} \right)^2 \ln \frac{w_n}{w_m} \right) \div 52 \]

where \( w_n \neq w_m \)

\[ = \frac{(29.5 \times 10^{-6})(2.54)}{(1.5 \times 10^{-3})(.005)} \left[ \frac{1}{2} 1 + \ln 2 \right] \div 52 = 37.11 \text{ m} \Omega \]

D) Resistance of ohmic collector

\[ R_O = \frac{\rho_{\text{Mo-Sn}}}{H} \left( \frac{L_O}{w_f - w_i} \right) \left[ \frac{1}{2} \frac{w_i}{(w_f - w_i)} + \left( \frac{w_i}{w_f - w_i} \right)^2 \ln \frac{w_f}{w_i} \right] \]

where \( w_f \neq w_i \)

\[ = \frac{(29.5 \times 10^{-6})(5.18)}{(1.5 \times 10^{-3})(.458)} \left[ \frac{1}{2} \frac{.152}{.458} + \left( \frac{.152}{.458} \right)^2 \ln \frac{.610}{.152} \right] \]

\[ R_O = 71.44 \text{ m} \Omega \]

Total resistance of contact pattern is:

\[ 3.48 + 4.59 + 37.11 + 71.44 = 116.62 \text{ m} \Omega \]
APPENDIX II

SPECIFICATIONS AND FORMAT A
SPECTROLAB, INC.

PROCESS SPECIFICATION

HIGH RESOLUTION, LOW COST SOLAR CELL CONTACT DEVELOPMENT

September 1, 1961

1. SCOPE

This specification describes the requirements necessary to obtain a collector grid on the P+ diffused silicon wafer using the Mid-Film process.

2. INPUT MATERIALS

2.1 Clean Back Surface Field Wafers

2.2 Silver printing powder

2.3 Mid-Film photosensitive resin

3. INPUT SUPPLIES

3.1 Photomasks

3.2 Long-nap pads or rollers for powder rub-out and cleaning.

3.3 1,1,1 Trichloroethane

3.4 #600 Scotch tape

4. EQUIPMENT AND FACILITIES

4.1 Equipment for applying resin (see 9.2).

4.2 Hg-Arc ultraviolet light source; collimated, capable of producing an intensity of about 30 mW/cm², for the 3650 A.U. line of Hg, on the surface of the wafer.

4.3 Equipment for deposition of metal powder and clean-off (see 9.3).

4.4 Firing equipment; to burn-off resin and mature silver powder at 600°C to 800°C, 40 to 60 seconds, air atmosphere.

4.5 Type A manufacturing space for above equipment

4.6 Utilities for above equipment

4.7 Heating, air conditioning, and equipment to comply with safety standards for above manufacturing space.
4.8 Waste disposal containers or recovery of solids (powder residues, paper, etc.) and liquids (waste solvents).

4.9 Pull test equipment.

5. THROUGHPUT AND LABOR CONTENT

Assuming round-the-clock (3 shifts/day) operation and 0.90 operating minutes per minute (see 9.1).

5.1 Output rate: 112 front contacted wafers (4 x 4)/operating minutes

5.2 Labor Content:

5.2.1 Semi-skilled Operator: 0.25 persons/shift

5.2.2 Maintenance: 0.1 persons/shift

6. PROCESS SEQUENCE AND PARAMETERS

6.1 Apply Mid-Film resin on front surface of wafers.

6.2 Expose to UV light through photomask.

6.3 Apply silver powder and develop pattern.

6.4 Clean-off and recycle excess powder.

6.5 Fire, air atmosphere, 575°C for 45 sec. to remove organics followed by a 675°C for 30 sec. to sinter powder.

6.6 Allow wafers to cool to room temperature.

6.7 Transfer wafers to next station.

7. BY-PRODUCTS

7.1 Chlorinated hydrocarbon vapors at resin application station (see 9.2).

7.2 Resin vapors during firing.

7.3 Cleaning solvent vapors when cleaning equipment.

7.4 Total estimated amount of fumes: 0.05 cu. ft./operating minute.

7.5 Silver powder for reclaim.

8. PRODUCT REQUIREMENTS AND Q.A.

8.1 In Line None. (Alludes to equipment in production machine that would signal malfunction.)

8.2 Q.A. Process Control Tests
8.2.1 Front Grid Pattern:

8.2.1.1 Silver must be adherent and be able to pass #600 Scotch tape test.

8.2.1.2 Should pass same test as above after 2 weeks of environmental exposure (70°C and 100% humidity). Ten test cells run once per week (10/162,000 frequency).

8.2.2 Ohmic solder pads:

8.2.2.1 Silver contact pad must be solderable with 62 Sn, 36 Pb, 2 Ag solder.

8.2.2.2 Silver contact pad should pass a 90° pull test of at least 500 grams when a #22 gauge solid copper wire is soldered to it. One test cell run once per hour (1/1350 frequency).

8.2.2.3 Should pass same test as above after 1 week of environmental exposure (70°C and 100% humidity). Ten test cells run once per week (10/162,000 frequency).

9. NOTES

9.1 Specification based on prototype equipment currently under development at Ferro Corp.

9.2 Spray, roller-coat, spin are procedures under consideration for application of resin. Chlorinated hydrocarbon vapors are heavier than air. Equipment will include collection of low-lying vapors. Resin is being applied by spinning in preparing the samples for Task I of the present contract.

9.3 Prototype to be developed.

Prepared by:

[Signature]

G. H. Johnson

GHJ/dmd
### SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

#### FORMAT A — PROCESS DESCRIPTION

| A-1 Process Reference | G MET |

Note: Names given in brackets [ ] are the names of process attributes requested by the SAMIS computer program.

| A.2 Descriptive Name of Process | Mid-Film Application of Grid Metallization |

#### PART 1 — PRODUCT DESCRIPTION

| A.3 [Product Reference] | Photovoltaic Wafer, Mid-Film Grid Applied |

| A.5 Unit of Measure [Product Units] | Wafer |

#### PART 2 — PROCESS CHARACTERISTICS

| A.6 [Output Rate] (Not Thruput) | 125/minute |

| A.7 [Input, Inventory, Time] | 7.0 Calendar Minutes (Used only to compute in process inventory) |

| A.8 [Duty, Cycle] | 0.9 Operating Minutes Per Minute |

| A.8a [Number, Of, Shifts, Per, Day] | 3.0 Shifts |

| A.8b [Personnel, Integration, Override Switch] | On (Off or On) |

#### PART 3 — EQUIPMENT COST FACTORS (Machine Description)

| A.9 Component [Referent] | Mid-Film Application Equip. |

| A.9a Component [Descriptive Name] | IR Furnace 4 units |

| A.10 Base Year For Equipment Prices [Price, Year] | 1979 1979 |

| A.11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of, and, $ Per Component) | $70,000.00 Est. * $140,000.00 Est. |

| A.12 Anticipated, [Useful, Life] (Years) | 10 years 7 years |

| A.13 [Salvage, Value] ($ Per Component) | $7,000.00 $12,000.00 |

| A.14 [Removal, And, Installation, Cost] ($/Component) | $3,000.00 $12,000.00 |

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, [1975 6 0 *], DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

*Prototype production equipment being built. Parts 2 and 3 are estimated on 4" wide conveyor.*

Rev. C 9/1/81
### PART 4: DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)

<table>
<thead>
<tr>
<th>Catalog Number</th>
<th>Amount Required</th>
<th>Units</th>
<th>Requirement Description or Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2064D</td>
<td>Floor Space-2720 sq. ft.</td>
<td>Class A Space</td>
<td></td>
</tr>
<tr>
<td>B3096D</td>
<td>1.00 person/shift</td>
<td>Semiconductor-assembler</td>
<td></td>
</tr>
<tr>
<td>B3736D</td>
<td>.40 person/shift</td>
<td>Maintenance Mechanic II</td>
<td></td>
</tr>
</tbody>
</table>

### PART 5: DIRECT REQUIREMENTS PER MACHINE PER MINUTE

<table>
<thead>
<tr>
<th>Catalog Number</th>
<th>Amount Required</th>
<th>Units</th>
<th>Requirement Description or Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2032D</td>
<td>18.75 cu. ft./min</td>
<td>Compressed Air</td>
<td></td>
</tr>
<tr>
<td>RG6933</td>
<td>34.4 gm./min.</td>
<td>Photo Sensitive Resin (70% utilization)</td>
<td></td>
</tr>
<tr>
<td>RH3666B</td>
<td>3.13 gm./min.</td>
<td>Metallic Powder (95% utilization)</td>
<td></td>
</tr>
<tr>
<td>C1032B</td>
<td>.688 KWH/min.</td>
<td>Power Required</td>
<td></td>
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</table>

### PART 6: INTRA-INDUSTRY PRODUCT(S) REQUIRED

<table>
<thead>
<tr>
<th>[Required, Product]</th>
<th>[Yield]*</th>
<th>[Total, Ratio]**</th>
<th>Units Out/Units In</th>
<th>Units Of A-26***</th>
</tr>
</thead>
<tbody>
<tr>
<td>B WAFER</td>
<td>1.00</td>
<td>wafers/wafers</td>
<td>Back Contacted Wafer</td>
<td></td>
</tr>
</tbody>
</table>

*100% minus percentage of required product lost in this process.  
**Assume 100% yield here.  
***Examples: Modules/Cells or Cells/Wafer.
Slide 74

HIGH RESOLUTION, LOW COST SOLAR CELL

CONTACT METALLIZATION

Calculations for SAMICS Format A

Production Rates

Prototype line speed - 50 feet per minute
30 wafers each 12 linear feet
50 x 30 = 125 wafers per minute maximum
12

90% operating time x 125 = 113 wafers production/min.

3 shifts, 8 hours each, 7 days per week operation
10,080 minutes x 113 = 1,139,040 wafers/week

Above calculations are based on present concept of a single line 4½" wide, proceeding through five work stations - 1. Spraying the Resin - 2. UV Curing - 3. Metal Powder Application - 4. Clean up and Recycling Excess Powder - 5. IR Belt firing. (5 lines, 4 furnaces)

Space Required

Length of prototype by station

1. Spray  - 80 ft²
2. UV  - 120"
3. Powder  - 60"
4. Clean-up  - 60"
5. IR Furnace (4 x 300 ft²) 1200"
Subtotal 1520 ft²

Estimated space for storage, servicing, etc. - 40'-long x 30' wide or 1200 sq. ft.
Total Area 2720 sq ft.

Compressed Air

15 c.f.m. at 40 p.s.i. line pressure max. for one spray gun.
15 = 0.15 cu.ft. compressed air per wafer

Power

Operating 4 IR furnaces 40,000 watts
Maching 500 watts
Air comp. 500 watts
41,000 W ÷ 7500 cells/hr = 0.005 kWh/cell
Material Usage

Wet Resin - 12 milligrams/sq. in. (4 milligrams/sq. in. dry resin)
- 4" x 4" wafer - 16 sq. in.
  \[16 \times 12 = 275 \text{ milligram/wafer}\]
  \[.70 \text{ (applied mtl.)}\]
- \[\frac{275 \text{ mg/wafer}}{1.34 \text{ g/cm}^3} = 205 \text{ microliters/wafer}\]

Metal Powder

Estimated silver usage per square inch coverage is 10 mg.
July 1, 1981

Spectrolab
12500 Gladstone Avenue
Sylmar, California 91342

Thank you for your interest in our Mid-Film process. We are pleased to quote you current prices on the following materials:

- MF5202 Mid-Film Ag 98% Powder: $0.99/gm. in 50,000 gm. quantities
- RG4933 Mid-Film Resin: 550 gallons $75.00/gal.
  - 1,100 " $65.00/gal.
  - 16,500 " $60.00/gal.

The price for MF5202 is based on the June 30 metal market price of $10.67/T.O. for silver. Any changes in the metal price will be reflected in the price of MF5202. Firm price for MF5202 is quoted on the date orders are placed.

If we can be of further assistance please call.

Sincerely yours,

COLOR DIVISION
Ferro Corporation

Raymond B. Jones
Business Development Manager

RBJ:md
### A.2 [Descriptive Name] of Process: Mid-Film Application of Grid Metallization

#### PART 1 — PRODUCT DESCRIPTION

<table>
<thead>
<tr>
<th>A3 [Product Referent]</th>
<th>G Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4 Descriptive Name [Product Name]</td>
<td>Photovoltaic Wafer, Mid-Film Grid Applied</td>
</tr>
<tr>
<td>A5 Unit of Measure [Product Units]</td>
<td>Wafer</td>
</tr>
</tbody>
</table>

#### PART 2 — PROCESS CHARACTERISTICS

<table>
<thead>
<tr>
<th>A6 [Output Rate] (Not Throughput)</th>
<th>125/minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>A7 [Inprocess Inventory Time]</td>
<td>7.0</td>
</tr>
<tr>
<td>A8 [Duty Cycle]</td>
<td>0.9</td>
</tr>
<tr>
<td>A9a [Number of Shifts Per Day]</td>
<td>2</td>
</tr>
<tr>
<td>A9b [Personnel Integration, Override Switch]</td>
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<td>A10 Best Year For Equipment Prices [Price Year]</td>
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<td>25 gm./min.</td>
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<tr>
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<td>1.35 KWH/min.</td>
<td></td>
<td>Power Required</td>
</tr>
<tr>
<td>E1416D</td>
<td>8.0 cu.ft./min.</td>
<td></td>
<td>Nitrogen Gas</td>
</tr>
<tr>
<td>E1336D</td>
<td>.0094 cu.H/min.</td>
<td></td>
<td>Hydrogen Gas</td>
</tr>
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*100% minus percentage of required product lost in this process.
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CONTACT METALLIZATION

Mo-Sn-TiH₂ Metallization

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Space Required

Length of prototype by station

1. Spray - 80 ft²
2. UV - 120"
3. Powder - 60"
4. Clean-up - 60"
5. IR Furnace (4 x 300 ft²) 1200" Subtotal 1520 ft²

Estimated space for storage, servicing, etc. = 40' long x 30' wide or 1200 sq. ft.
Total area 2720 sq. ft.

Compressed Air

15 c.f.m. at 40 p.s.i. line pressure max. for one spray gun.
15 = 0.15 cu.ft. compressed air per wafer

100

Power

Operating 4 IR furnaces 80,000 watts

Maching 500 watts

Air Comp. 500 watts

81,000 W ÷ 7500 cells/hr = 0.0108 kwh/cell
Material Usage

Wet Resin - 12 milligrams/sq.in. (4 milligrams/sq.in. dry resin)

- 4" x 4" wafer - 16 sq. in.

\[
\frac{16 \times 12}{.70 \text{ (applied mtl.)}} = 275 \text{ milligram/wafer}
\]

- 275 mg/wafer = 205 microliters/wafer

Metal Powder

Estimated metal usage per square inch coverage is 7.5 mg.

Price on Materials, Small Quantities

(Sylvania 280-325) Molybdenum Powder = $18.50/lb.
(Atlantic Equipment Engineers Sn266) Tin Powder = $50.00/lb.
(Ferro Corporation FX41) Titanium Hydride = $36.00/lb.