INK-JET PRINTING OF SILVER METALLIZATION FOR PHOTOVOLTAICS

PURDUE UNIVERSITY

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Nozzle Assembly (side view)

SCREW PLATE (lifted up)

CLIP SPRING

RETIrNING CLIP

METAL PLATE WITH DROP FORMING HOLES

PLastic "O" METAL FINE PLATE RING PLATE PLASTIC SCREEN
Nozzle Assembly (front view)

Flow Diagram of Ink-Jet Printer System
Computer Controlled Ink-Jet Printer

Print Head and Substrate Mount
Ink Requirements

1. No Particulates
2. Low Viscosity
3. High Surface Tension
4. High Inorganic Content
5. Non Clogging
6. Stable

Ink Chemistry

1. Silver Compound
   Ag neodecanoate

2. Adhesion Agent
   Bi 2-ethylhexanoate

3. Solvent
   toluene or xylene

4. Stabilizer
   neodecanolic acid
Ink-Jet Printing Studies

**Ink Parameters**
1. viscosity
2. surface tension
3. metal content
4. solvent vapor pressure

**Printer Parameters**
1. pulse voltage
2. pulse frequency
3. ink pressure
4. nozzle diameter
5. nozzle-substrate separation

**Substrate Parameters**
1. velocity
2. temperature

**Firing Parameters**
1. heating rate
2. maximum temperature
3. time at maximum temperature
Diagram of the Ink-Jet Model

- To the ink reservoir
- Piezoelectric material
- Piezoelectric transducer cavity
- Capillary tube
Ink-Jet Theory

\[ q_r = \pi r f T \frac{R^2}{8 \eta L} \left[ 1 - \frac{1}{2} \left( \frac{R}{r} \right)^2 \right] \left[ \frac{1}{2} \eta - \frac{2 \eta \cos \theta}{r} \right] \]

**Ink Parameters**
- \( \gamma \) = surface tension
- \( \theta \) = contact angle
- \( \eta \) = viscosity

**Mechanical Parameters**
- \( r' \) = nozzle radius
- \( r_0 = 2r' \)

**Electrical Parameters**
- \( V \) = pulse voltage
- \( T \) = pulse duration
- \( f \) = pulse frequency

\( R, K, L, C \) and \( n \) are constant for a given printer.
Relationship of Ink-Flow Rate and Ink Viscosity

![Graph](image)

- Theory
- Experiment
Relationship of Ink-Flow Rate and Nozzle Diameter
Relationship of Ink-Flow Rate and Pulse Voltage Applied to the Piezoelectric Transducer
PROCESSING

Relationship of Ink-Flow Rate and Frequency of Pulses to the Piezoelectric Driver

![Graph showing relationship between ink flow rate and frequency of pulses]

Thermal Processing

Belt Furnace

$T_{\text{max}} = 280^0 \text{ to } 400^0 \text{C}$

cycle time = 40 - 70 minutes

Thermal Spike

$750^0 \text{ to } 850^0 \text{C}$

45 to 180 seconds
Thermal Effects on Performance of Thin-Film (Control) Solar Cells

- Belt Furnace Firing (50 min.)
- 1 min. Thermal Spiking
- 2 min. Thermal Spiking
- 3 min. Thermal Spiking

- Cell Con 227-1
- Cell Con 227-2
- Cell Con 227-3
Fired Film Properties

Composition

99% Ag - 1% Bi₂O₃

Adhesion

excellent (Scotch tape)

Solderability

excellent (100% acceptance)

Solder Leach Resistance

excellent (30 second dip)
Height Versus Width of Metal Fingers

Before Firing

After Firing
### Measured Finger-to-Finger Resistances (R_{ff}) and Series Resistance (R_{SE})

Calculated from I-V Curves for Solar Cells with Different Processing

<table>
<thead>
<tr>
<th>No. of Layers of An</th>
<th>Thermal Treatment Sequence(s)</th>
<th>JPL Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) B4605B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2) B6054B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) B6054B</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(4) B6054B×15S</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5) B6054B×15S</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R_{ff} R_{SE}</td>
<td>R_{ff} R_{SE}</td>
</tr>
<tr>
<td>5</td>
<td>9.38 ± 1.22 10.05 ± 1.79</td>
<td>8.26 ± 0.13 8.13 ± 0.42</td>
</tr>
<tr>
<td>10</td>
<td>5.52 ± 0.35 7.98 ± 0.39</td>
<td>7.76 ± 0.18 7.16 ± 0.48</td>
</tr>
<tr>
<td>20</td>
<td>2.44 ± 0.12 4.35 ± 1.77</td>
<td>1.65 ± 0.05 3.40 ± 0.71</td>
</tr>
</tbody>
</table>

(a) thermal treatments

- B = belt furnace with 70 minute cycle and 300°C maximum temperature
- 60S = sixty seconds at 800°C
- 15S = fifteen seconds at 800°C

(b) calculated from the I-V curves supplied by JPL

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### Current-Voltage Curve for 20-Layer Cell 114-3 After Thermal Treatment Step 4

**GRAPHICS PLOT**

*TEST 227-114-3 011796*

<table>
<thead>
<tr>
<th>( I (\text{mA}) )</th>
<th>( P ) (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100.0</td>
<td>50.00</td>
</tr>
<tr>
<td>-10.00</td>
<td>5,000</td>
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<tr>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>10.00 div</td>
<td>5,000/div</td>
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<td>50.00</td>
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<tr>
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<td>1.000</td>
</tr>
<tr>
<td>10.00 div</td>
<td>5,000/div</td>
</tr>
</tbody>
</table>

**Variables:**

- \( V_F \) - Ch3
- Linear sweep
- Start: 0.0000V
- Step: 0.0000V
- Constant: \( v \) - Ch1 0.0000V

**Constants:**

- \( I_{sc} \) = -61.38 mA
- \( V_{oc} \) = 0.5540 V
- \( P_{mp} \) = 20.2 mW
- \( I_{mp} \) = -52.6 mA
- \( V_{mp} \) = 385.0 mV
- \( A_{ff} \) = 5.11%
- Cell Area = 4 cm²
- Fill Factor = 0.595

**Notes:**

- R_{SE} = 2.082 Ω
- R_{ff} = 2.37 Ω

**Current-Voltage Curve for 20 Layer Cell 114-3 After Thermal Treatment Step 4.**
Effect of Quality of the Metal Film on Solar Cell Quality

(a) Cell 227-15 Poor Metal Film and Poor Solar Cell

(b) Cell 227-14 Good Metal Film and Good Solar Cell
Comparison of Series Resistance (R_{SE}) and Fill Factor (FF) for Solar Cells Metallized with MOD Silver With and Without a Ti/Pd Underlayer

<table>
<thead>
<tr>
<th>No. of Layers of Ag</th>
<th>B + 60S</th>
<th>B + 60S + 8</th>
<th>JPL Control Cells</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>R_{SE}</td>
<td>FF</td>
<td>R_{SE}</td>
</tr>
<tr>
<td>5</td>
<td>39.78</td>
<td>±0.09</td>
<td>32.67</td>
</tr>
<tr>
<td></td>
<td>±0.22</td>
<td>±0.79</td>
<td>±0.07</td>
</tr>
<tr>
<td>10</td>
<td>20.04</td>
<td>±0.14</td>
<td>1.75</td>
</tr>
</tbody>
</table>

(a) thermal treatments

B = belt furnace with 70 minute cycle and 300°C maximum temperature
60S = sixty seconds at 800°C

Seven Factors that Contribute to the Measured Series Resistance of a Solar Cell

![Diagram]

R_1 = Back Contact  
R_2 = Bulk  
R_3 = Diffused Layer  
R_4 = Front Contact  
R_5 = Grid Lines  
R_6 = Bus Lines  
R_7 = Measuring Circuit

R_{SE} = \sum_{i=1}^{7} R_i
Summary

1. A computer controlled ink jet printing system was developed.
2. A theoretical model which adequately describes the ink jet printer was developed.
3. A MOD silver ink was developed for use with the printer.
4. Grid patterns with suitably low sheet resistance can be produced.
5. Line definition to 50 µm can be achieved.
6. Good adhesion and solder leach resistance was demonstrated.
7. The contact resistance must be reduced in order to produce high efficiency cells.