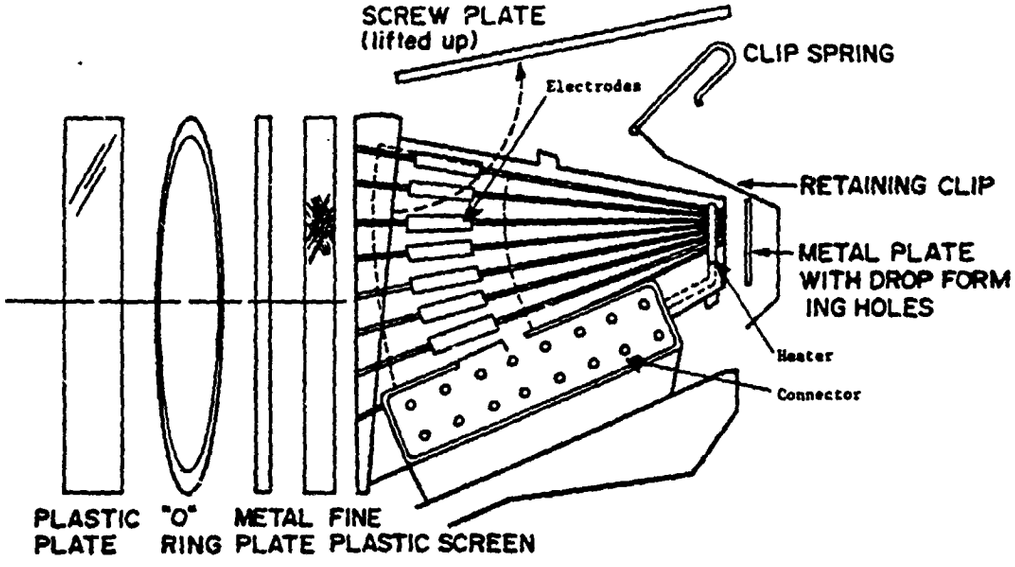
N87-16421

# INK-JET PRINTING OF SILVER METALLIZATION FOR PHOTOVOLTAICS

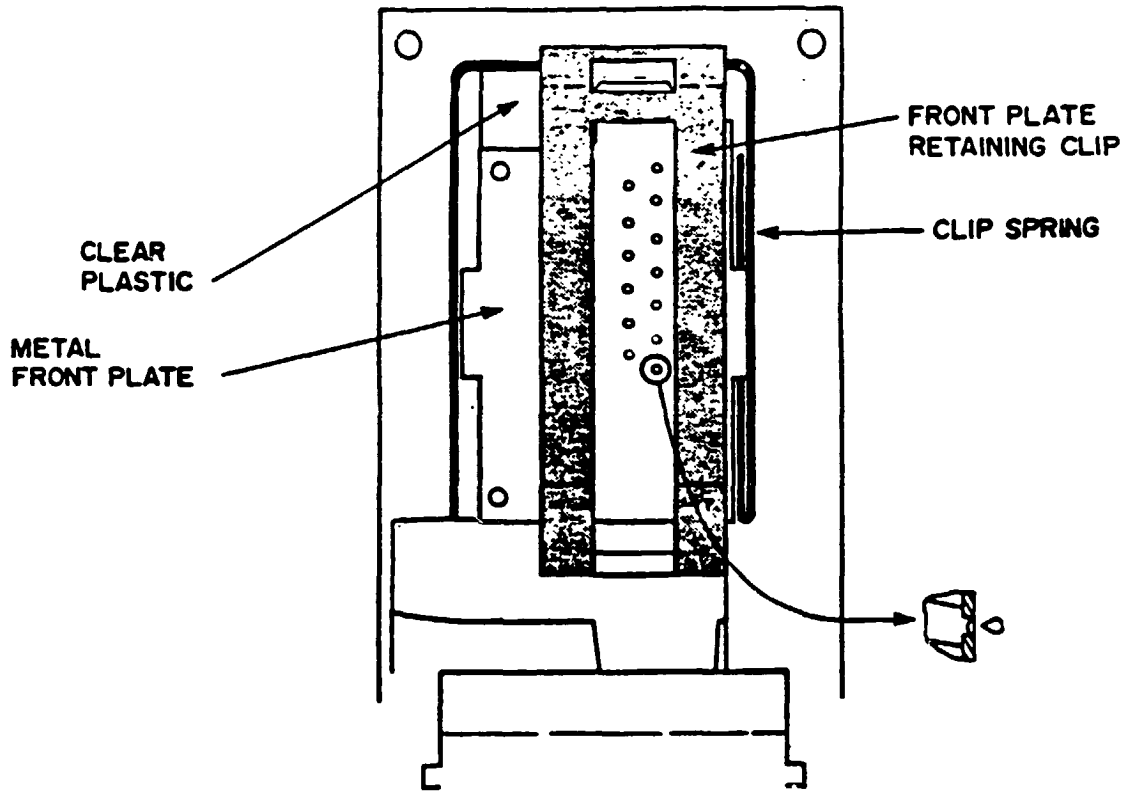
PURDUE UNIVERSITY

R. W. Vest

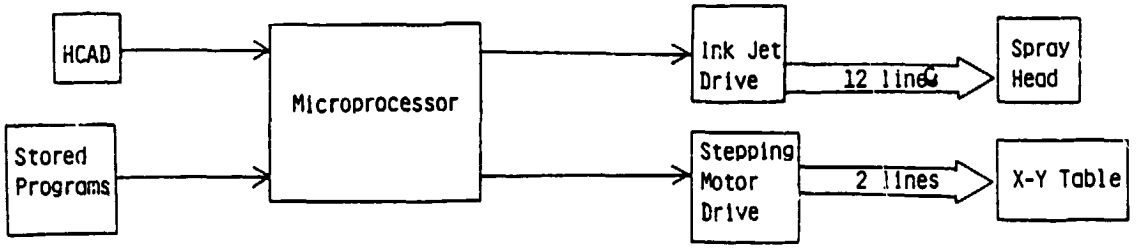
Nozzle Assembly (side view)



## 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

   neodecanoic 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

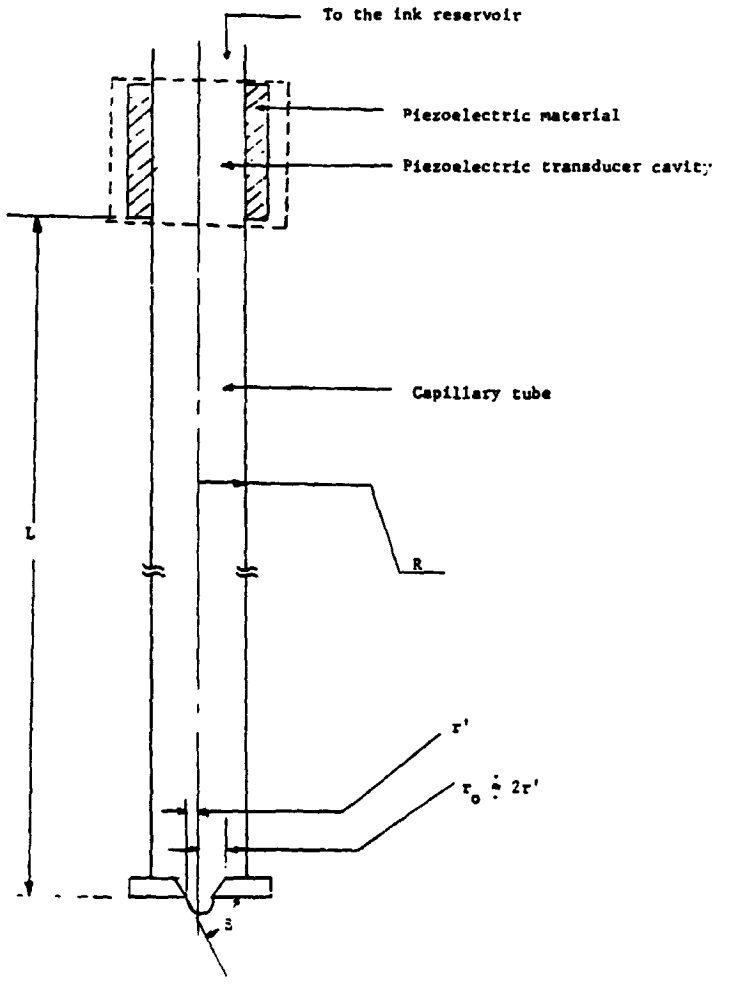
Substrate Parameters

1. velocity
2. temperature

Firing Parameters

1. heating rate
2. maximum temperature
3. time at maximum temperature

## Diagram of the Ink-Jet Model



# Ink-Jet Theory

$$Q_r = fT \frac{\pi R^2 r_0^2 K}{8\mu L}\left[1 - \frac{1}{2}\left[\frac{r_0}{R}\right]^2\right]\left[cV^n - \frac{2\sigma\cos\beta}{r'}\right]$$

Ink Parameters

- $\sigma$ = surface tension
- $\beta$ = contact angle
- $\mu$ = viscosity

Mechanical Parameters

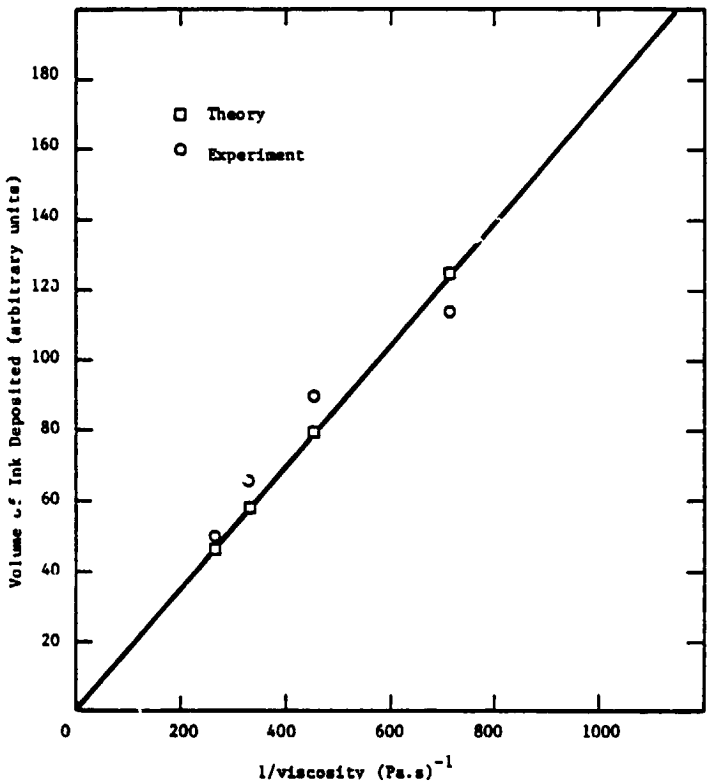
- $r'$ = nozzle radius
- $r_0 = 2r'$

Electrical Parameters

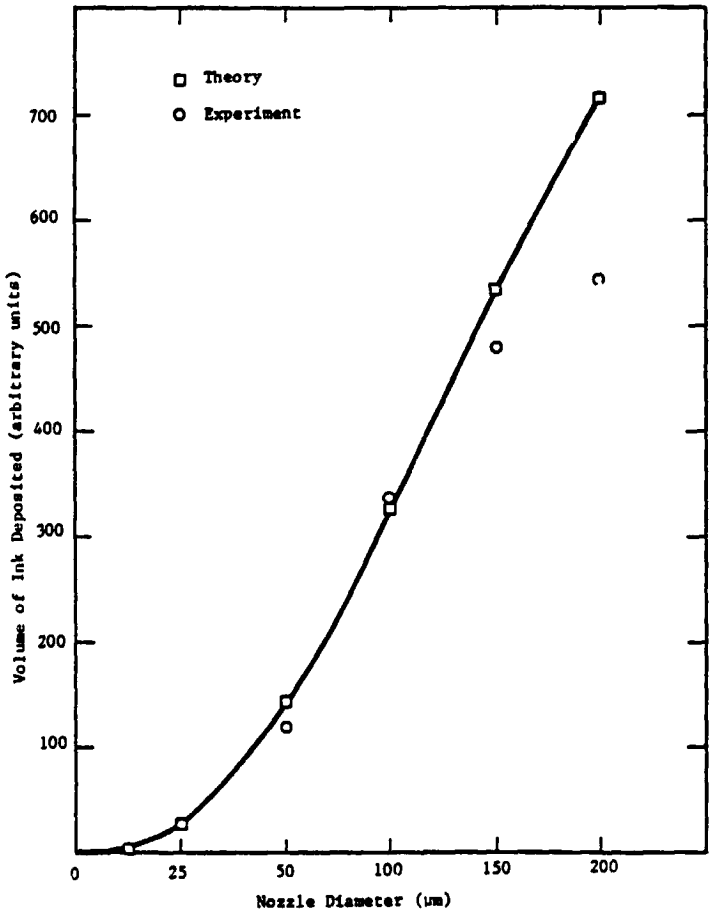
- V = pulse voltage
- T = pulse duration
- f = pulse frequency

R, K, L, C and n are constant for a given printer.

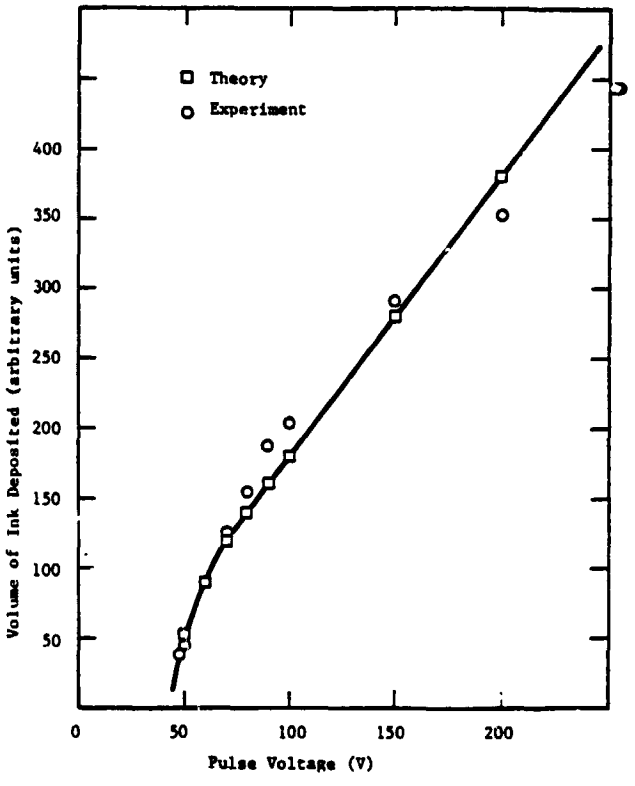
## Relationship of Ink-Flow Rate and Ink Viscosity



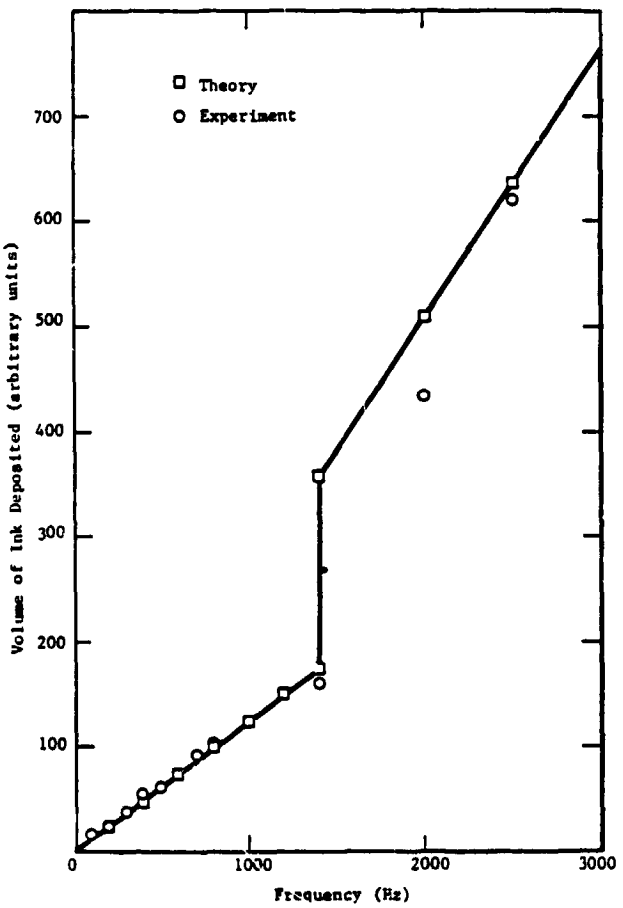
## Relationship of Ink-Flow Rate and Nozzle Diameter



## Relationship of Ink-Flow Rate and Pulse Voltage Applied to the Piezoelectric Transducer



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




## Thermal Processing

Belt Furnace

$T_{max}$ = 280° to 400°C

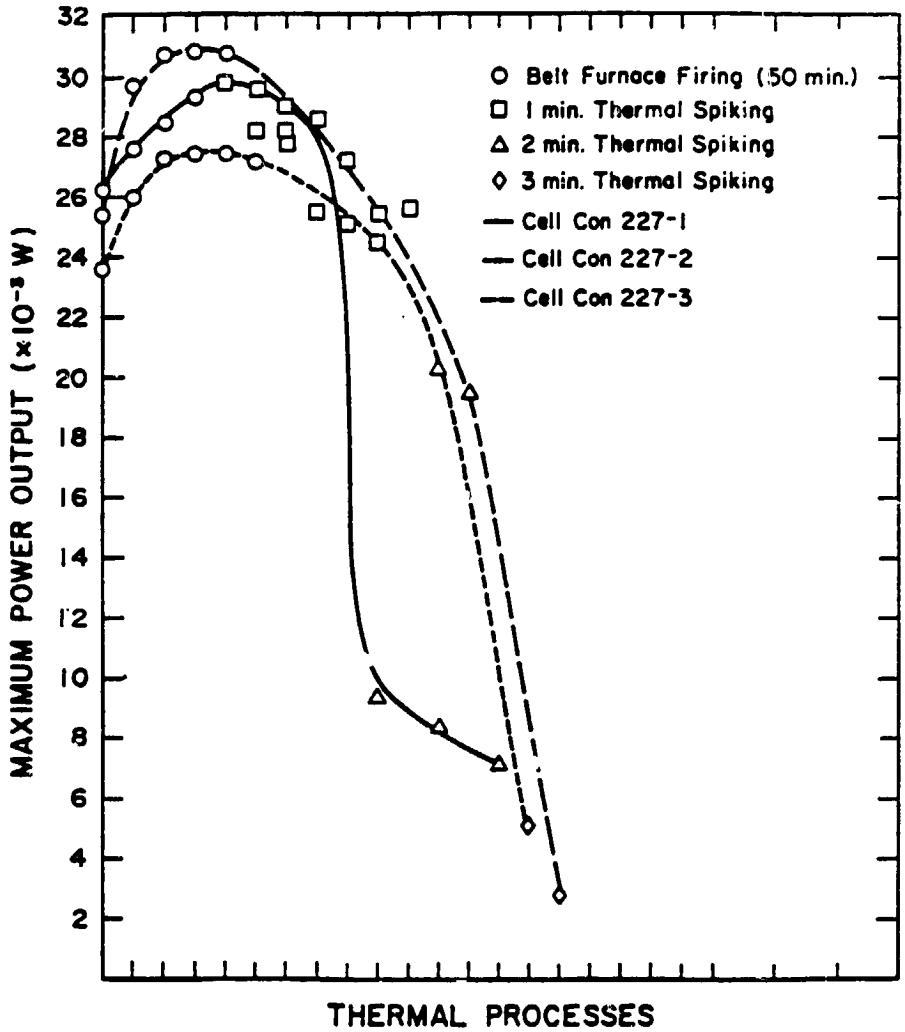
cycle time = 40 - 70 minutes

Thermal Spike

750° to 850°C

45 to 180 seconds

## Thermal Effects on Performance of Thin-Film (Control) Solar Cells



# Fired Film Properties

Composition

99% Ag - 1% $Bi_2O_3$

Adhesion

excellent (Scotch tape)

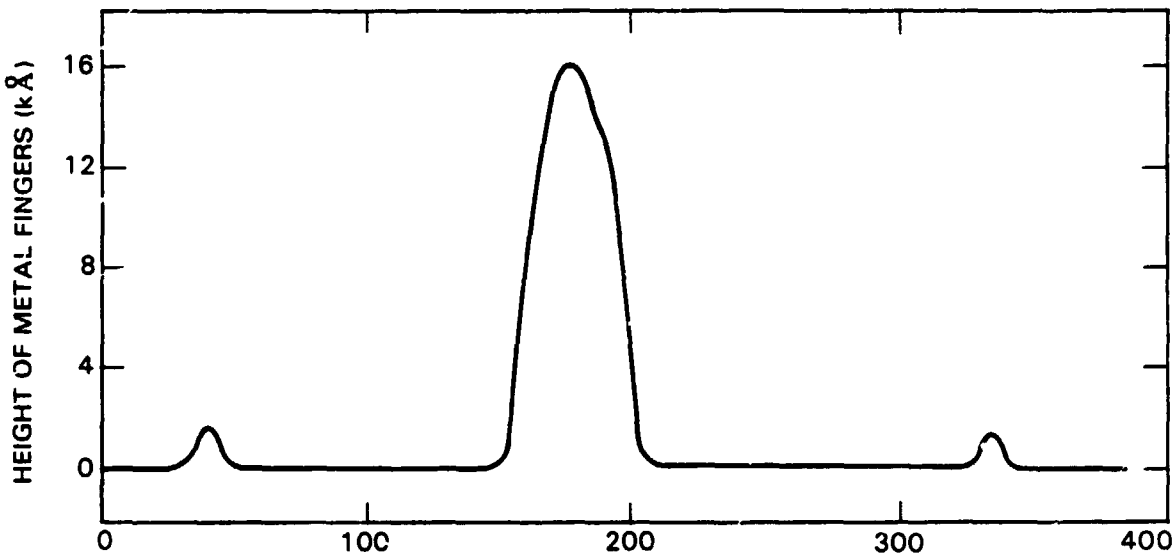
Solderability

excellent (100% acceptance)

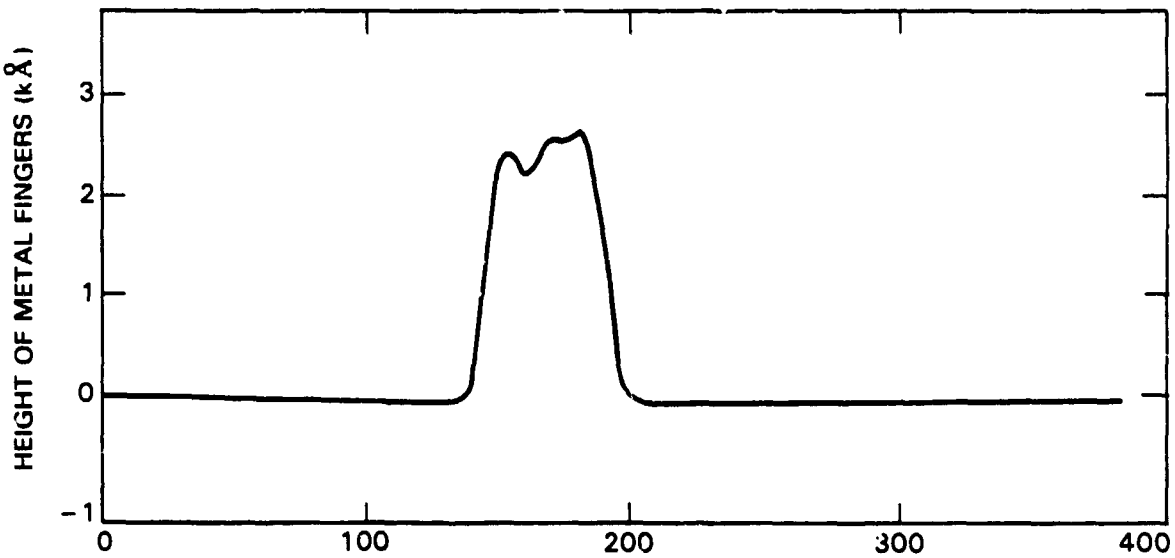
Solder Leach Resistance

excellent (30 second dip)

## Height Versus Width of Metal Fingers




**BEFORE FIRING**




**AFTER FIRING**

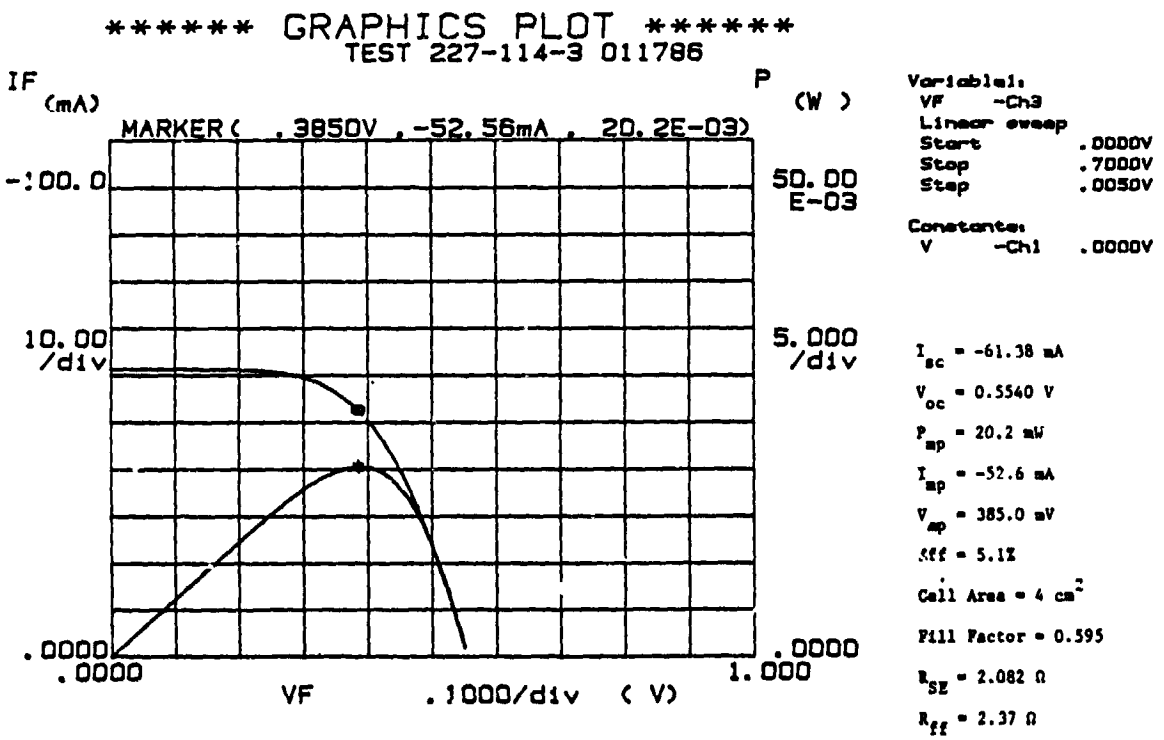
## Measured Finger-to-Finger Resistances ($R_{ff}$) and Series Resistance ($R_{SE}$) Calculated from I-V Curves for Solar Cells with Different Processing

| No. of Layers of Ag | Thermal Treatment Sequence[a] (1) B+60S | | (2) B+60S+B | | (3) B+60S+B$^2$ | | (4) B+60S+B$^2$+15S | | (5) B+60S+B$^2$+15S$^2$ | | JPL Control Cells | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R_{ff}$ | $R_{SE}$ | $R_{ff}$ | $R_{SE}$ | $R_{ff}$ | $R_{SE}$ | $R_{ff}$ | $R_{SE}$ | $R_{ff}$ | $R_{SE}$ | $R_{ff}$ | $R_{SE}$ |
| 5 | 9.38 ±1.22 | 10.05 ±1.79 | 8.26 ±0.13 | - | 8.13 ±0.42 | 9.48 ±1.33 | 8.76 ±0.59 | 10.92 ±0.67 | 8.57 ±0.40 | 10.59 ±1.57 | | |
| 10 | | | 5.52 ±0.35 | - | 5.13 ±0.39 | 7.98 ±0.89 | 3.43 ±0.18 | 7.16 ±0.48 | 3.41 ±0.18 | 6.73 ±0.43 | | |
| 20 | | | | | | | 2.44 ±0.12 | 4.35 ±1.77 | 1.65 ±0.05 | 5.40 ±0.71 | | |
| | | | | | | | | | | | 5.22 ±1.32 | 1.49 ±0.09 |
| | | | | | | | | | | | | 0.63[b] ±0.12 |

(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

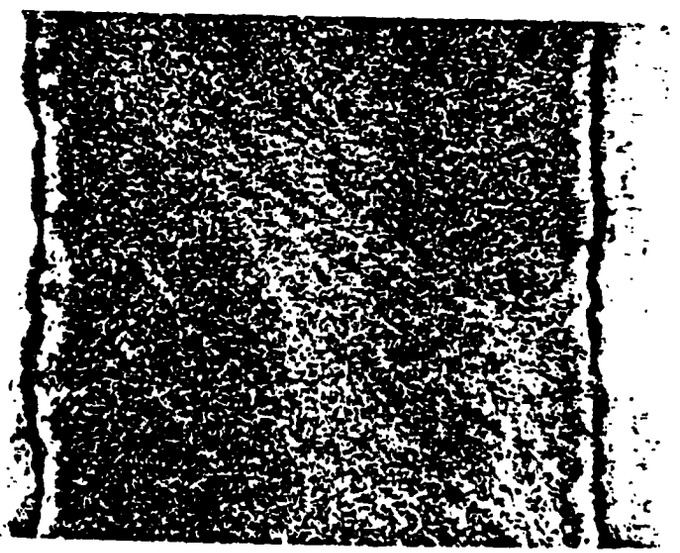
## Current-Voltage Curve for 20-Layer Cell 114-3 After Thermal Treatment Step 4




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



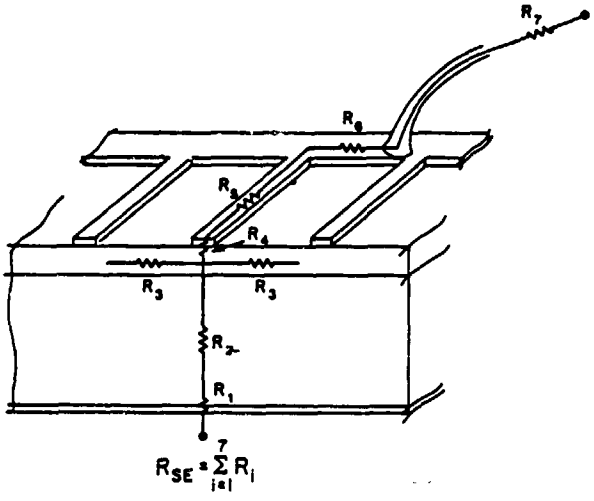
(b) Cell 227-14 Good Metal Film and Good Solar Cell

## Comparison of Series Resistance ($R_{SE}$) and Fill Factor (FF) for Solar Cells Metallized with MOD Silver With and Without a Ti/Pd Underlayer

| No. of Layers of Ag | Thermal Treatment Sequence(a) | | | | | | | | JPL Control Cells | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B + 60S | | | | B + 60S + B | | | | | | | |
| | No Ti/Pd | | With Ti/Pd | | No Ti/Pd | | With Ti/Pd | | Purdue Data | | JPL Data | |
| | $R_{SE}$ | FF | $R_{SE}$ | FF | $R_{SE}$ | FF | $R_{SE}$ | FF | $R_{SE}$ | FF | $R_{SE}$ | FF |
| 5 | 39.78 ±10.09 | 0.22 ±0.02 | 2.48 ±0.79 | 0.51 ±0.07 | 32.67 ±15.15 | 0.24 ±0.02 | 1.78 ±0.25 | 0.57 ±0.04 | | | | |
| 10 | | | | | 20.04 ±3.12 | 0.24 ±0.01 | 1.75 ±0.41 | 0.58 ±0.03 | | | | |
| | | | | | | | | | 1.70 ±0.36 | 0.56 ±0.04 | 0.69 ±0.04 | 0.65 ±0.03 |

(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




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

$R_1$ = 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

## 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.