285-
10/13/78

16.599
DOE/JPL/954868-2

AUTOMATED ARRAY ASSEMBLY, PHASE II

Quarterly Report No. 2, January 1—March 31, 1978

By
R. V. D'Aiello

March 1978

Work Performed Under Contract No. NAS-7-100-954868

RCA Laboratories
Princeton, New Jersey

U.S. Department of Energy

MASTER

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$5.25
Microfiche \$3.00

DRL Line Item No. 10

AUTOMATED ARRAY ASSEMBLY, PHASE II

R. V. D'Aiello
RCA Laboratories
Princeton, New Jersey 08540

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

QUARTERLY REPORT NO. 2

March 1978

MASTER

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the Department of Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

Prepared Under Contract No. 954868 For
JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91103

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report contains information prepared by RCA Corporation under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, the National Aeronautics and Space Administration, or the Department of Energy.

PREFACE

This Quarterly Report, prepared by RCA Laboratories, Princeton, NJ 08540, describes the results of work performed from January 1, 1978 to March 31, 1978 in the Energy Systems Research Laboratory, B. F. Williams, Director; Materials and Process Laboratory, Solid State Division, Somerville, NJ, H. Veloric, Manager; and at the Advanced Technology Laboratory, Government and Commercial Systems, Camden, NJ, F. E. Shashoua, Director. The Project Scientist is R. V. D'Aiello and the Project Supervisor is D. Richman, Head, Semiconductor Materials Research. Others who participated in the research and writing of this report are:

J. Toner	-	cost analysis
D. Richman	-	silicon material
G. Schnable	-	metallization and AR coating
W. Kern	-	
K. Bube	-	
R. Scott	-	panel design and fabrication
M. Crouthamel	-	
H. Veloric	-	
F. Mayer	-	manufacturing
U. Roundtree	-	
L. Guarino	-	

The JPL Task Manager is Don Bickler.

TABLE OF CONTENTS

Section	Page
I. SUMMARY	1
II. INTRODUCTION	2
III. PROGRESS	4
A. Junction Formation	4
1. Ion Implantation	4
2. POCl_3 Diffusion	6
B. Screen-Printed Metallization	7
1. Ink Analysis - Commercial	7
2. Ink Synthesis - RCA	12
3. Ink-Electrical Conductivity	12
4. Laser Heating of Screen-Printed Line	25
5. Screen-Printing Parameters	26
6. Solar-Cell Metallization Diagnostics	28
C. AR Coating	31
1. AR Coating Materials Parameters for Spray Solution System	31
2. Variables of Spray Deposition Equipment	36
3. Solar-Cell Surface Conditions Before Coating	37
4. Properties of the AR Coating	37
5. Heat Treatment Effects	38
6. Conclusions	40
D. Interconnect and Panel Assembly	42
1. Welding Evaluation	42
2. Soldering Evaluation	43
3. Panel Lamination - PVB Process	44
4. Panel Lamination - Acrylic Casting	45
IV. PLANS FOR NEXT QUARTER	47
A. Junction Formation	47
1. POCl_3 Diffusion	47
2. Ion Implantation	47
B. Screen-Printed Metallization	47
C. Spray-on Antireflection Coating	47
D. Soldering Technology	47
E. PVB Laminating	48
F. Acrylic Encapsulation	48

LIST OF ILLUSTRATIONS

Figure	Page
1. Major steps of process sequence	3
2. Spectral response of gettered and nongettered ion-implanted solar cells	5
3. Effect of implant dosage on solar-cell efficiency	5
4. Effect of implant dosage on V_{oc}	6
5. Effect of various ion implants on solar-cell efficiency	7
6. Firing time-temperature dependence on sheet resistance of screen-printed Metz K-150 silver ink	16
7. Firing time-temperature dependence of resistivity of screen-printed Metz K-150 silver ink	16
8. Effect of coefficient of variation of various screen-printing parameters	27
9. Applied force as a function of squeegee compression in screen printing	28

LIST OF TABLES

Table	Page
1. Processing Parameters for POCl_3 Diffusion	8
2. Emission Spectrographic Analyses of Thick-Film Cation Constituents (ppm by weight)	10
3. Emission Spectrographic Analysis of Thick-Film Cation Constituents (ppm by weight)	11
4. Emission Spectrographic Analysis of Silver Powder Cation Constituents (ppm by weight)	13
5. Emission Spectrographic Analyses of Cellulosic Polymers Cation Constituents (ppm by weight)	14
6. Frit Properties	15
7. Percent of Bulk Electrical Conductivity of RCA Ag Inks (No Frit) .	17
8. Percent of Bulk Electrical Conductivity of RCA - Metz Ag vs Frit Content	18
9. Percent of Bulk Electrical Conductivity of Commercial Inks	20
10. Emission Spectrographic Analysis of Thick-Film Cation Constituents (ppm by weight)	24
11. Percent of Bulk Electrical Conductivity	25
12. Solar-Cell Characteristics Evaporated Metal Control vs Screen- Printed Metal	29
13. Electron-Probe Microanalysis of Ag-Ink Lines on Solar-Cell Wafers.	30
14. Solvent Systems Evaluated for Titania-Silica AR Spray Coatings . .	33
15. Summary of Results from Zicon Spray Tests for AR Coating	35
16. Typical Optical Properties of Sprayed vs Spun AR Coatings	39
17. Typical Optical Properties of AR Coatings as a Function of Heat Treatments	41

SECTION I

SUMMARY

During the second quarter of this effort we have concentrated on our studies of junction formation by ion implantation, metallization by silk screen printing, spray-on antireflection (AR) coating, and interconnections by welding and reflow solder.

Our ion-implantation studies have shown that the cell efficiency and open-circuit voltage increase with increasing ^{31}P up to 5×10^{15} ion dosage. This is the highest dose we have used to date. At this dosage efficiencies of just under 15% have been obtained.

The metallization studies have been concerned with the characterization of commercially obtained inks as well as the in-house synthesis of several inks. To date we have had limited success with screen printing the front-side metallization pattern. It appears that phosphorus is a necessary component of the ink in order to obtain low contact resistance. However, the interaction of the ink with the silicon surface is not well understood and much more work must be done in this area.

The spray-on AR coating studies have resulted in the definition of a series of process steps which yield an AR coating of satisfactory uniformity in thickness and reproducibility from run to run. Some particulate formation occurs in the liquid which constitutes a source of contamination, but the problem is mainly a cosmetic one. The overall efficiency of typical cells is increased by a factor of 1.4, from 7.9% uncoated to 11.2% after spray coating.

We have concluded on the basis of our present studies that welding is not a suitable assembly process for cells of current design and have gone to a solder reflow technique.

As an alternate to the PVB lamination technique we have begun to look at casting methyl methacrylate-butyl acrylate resin between the glass plates. This system is less expensive than PVB but requires developing a technique of curing the resin which allows for the 20% volume shrinkage which occurs on curing without creating bubbles between the glass sheets. Our approach to solving this problem is described in Section III of this report.

SECTION II

INTRODUCTION

The purpose of our overall program is to establish technological readiness and provide verification for the elements of a manufacturing sequence which would ultimately be suitable for the large-scale production of silicon solar-array modules at a selling price of less than \$500/kW. A program and process plan for accomplishing this objective was developed and put into operation during the first quarter. This plan is centered around the processing sequence shown in Fig. 1. Three junction-formation processes are shown; since our cost analysis shows that they do not differ greatly in cost, each should be considered for technical merits and possible future cost reduction. In Section III the progress made in the various process steps of the plan is described, and plans for the next quarter are summarized in Section IV.

Figure 1. Major steps of process sequence.

SECTION III

PROGRESS

A. JUNCTION FORMATION

1. Ion Implantation

The results of our studies given in the previous quarterly report [1] showed that incorporation of a gettering step along with ion implantation yielded a significant increase in the efficiencies of the resultant cells. This gettering process consists of deposition of a boron glass on the backside of the wafer after implantation and silane capping of the n^+ layer. The glassed wafer is then annealed to remove implantation damage. The highly conducting boron glass is left on the backside of the wafer. The effect of this process on increasing the long wavelength response of an ion-implanted cell is shown in Fig. 2. Here the quantum efficiency vs wavelength data for a cell implanted on both sides is compared with a gettered-implanted cell. The large increase in quantum efficiency in the long wavelength region for the gettering cell is readily apparent. This higher quantum efficiency indicates that diffusion lengths of 200 to 350 μm are obtained even after the high-temperature annealing step.

We have incorporated gettering as a standard part of the ion-implantation process and have begun to study a number of variables as a function of dose and annealing temperature. In Fig. 3 we show the efficiency of the completed cell as a function of ^{31}P dose. Note that the efficiency appears to be increasing with increasing dose and that efficiencies approaching 15% have been achieved with both 1000°C and 900°C anneals. Figure 4 shows the open-circuit voltage (V_{oc}) as a function of the same variables. Here again the V_{oc} improves with increasing dose. The 1000°C anneal appears to give a smoother increase in V_{oc} (the 5×10^{15} dose excepted) than the 900°C anneal. These voltages are still lower than those for high quality diffused cells. This is probably partly

1. R. V. D'Aiello, *Automated Array Assembly, Phase II*, Quarterly Report No. 1, prepared under Contract No. 954868 for Jet Propulsion Laboratory, December 1977.

Figure 2. Spectral response of gettered and nongettered ion-implanted solar cells.

Figure 3. Effect of implant dosage on solar-cell efficiency.

Figure 4. Effect of implant dosage on V_{OC} .

dose-dependent and partly anneal-dependent. In the next quarter we shall investigate the effect of higher doses on V_{OC} as well as multiple step, low-temperature annealing.

Finally, we have looked at the effect of implanting with both ^{75}As and ^{31}P vs ^{31}P alone. As shown in Fig. 5 we have not seen a significant difference in the efficiency as a function of the implant species.

2. POCl_3 Diffusion

We have now run more than 50 lots of wafers (10 to 50 wafers/lot) with various diffusion parameters. These runs are shown in Table 1. Selected wafers from each lot have been reserved as standards for evaporated metal contacts. The remainder of the wafers shall be used for screen printing of the metallization. The optimization of this junction-formation process for cell performance has temporarily been superseded by the requirements of the screen-printing process as discussed in the next section.

Figure 5. Effect of various ion implants on solar-cell efficiency.

B. SCREEN-PRINTED METALLIZATION

1. Ink Analysis - Commercial

In addition to the phosphorus-bearing OI-6105* ink, supplemental Ag and Ag/Al inks were obtained from Engelhard** and Thick Film Systems†. The inks containing glass frit are Engelhard E-422-C (Ag), E-422-E (Ag), E-422-D (Ag/Al), E-422-F (Ag/Al), and Thick Film Systems 3347 (Ag). A fritless Ag ink, Thick Film Systems A250, was also acquired.

The emission spectrographic analyses, listed in Table 2, indicates that the frit-bearing inks are generically lead borosilicate in composition with varying proportions of the three major oxides PbO, B₂O₃, and SiO₂. The remaining elements are present in trace quantities and are brought in by impurities in the raw materials and/or ball-mill grinding of the frit. The solids content of the inks ranged from 78 to 83 wt pct.

*Owens-Illinois, Inc., Toledo, OH.

**Engelhard Industries, East Newark, NJ.

†Thick Film Systems, Inc., Santa Barbara, CA.

TABLE 1. PROCESSING PARAMETERS FOR POCl_3 DIFFUSION

Lot No.	POCl_3 (°C)	N_2 (CFH)	O_2 (CFH)	POCl_3 Carrier O_2 (CFH)	POCl_3		Deposit (min)	Drive (min)	Pull (min)	Temp (°C)
					Push (min)	Warm (min)				
033	20	5	.5	.5	15	10	20	30	10	850
034	0	5	.5	.5	10	10	45	10	10	850
035	0	5	.5	.5	10	10	45	10	10	850
036	0	3.9	.35	.35	10	20	20	30	10	850
037	0	3.9	.35	.35	10	20	20	30	10	850
038	0	3.9	.35	.35	10	20	20	30	10	850
039	0	5	.5	.5	10	10	20	30	10	850
040	0	5	.5	.5	10	10	20	30	10	850
041	0	5	.5	.5	10	10	20	30	10	850
042	0	5	.5	.5	10	10	20	30	10	850
043	0	5	.5	.5	10	10	20	30	10	850
044	0	5	.5	.5	10	10	20	30	10	850
046	0	5	.5	.5	10	10	20	30	10	850
047	20	5	.5	.5	15	10	20	30	10	850
048	3	5	.5	.5	20	10	20	30	4	850
049	-6	5	.5	.5	10	10	20	25	10	850
050	0	5	.5	.5	15	10	20	25	10	850
051	0	5	.5	.5	15	10	20	22	10	850
055	0	5	.5	.5	15	10	20	22	10	
056	0	5	.5	.5	15	10	20	22	10	
057	26	5	.05	.5	15	10	20	30	10	850
058	26	5	.05	.5	15	10	20	30	10	850
059	25	5	.05	.5	15	10	20	30	10	850
060	26	5	.05	.5	15	10	20	22	10	850
061	0	5	.5	.5	15	10	20	22	10	
062	0	5	.5	.5	15	10	20	20		
064	30	5	.05	.5	15	10	20	30	10	850
065	30	5	.05	.5	15	10	20	30	10	850
066	26	5	.05	.5	15	10	20	30	10	850
069	30	5	.05	.5	15	10	20	30	10	850
070	26	5	.02	.5	15	10	20	30	10	850
071	26	5	.02	.5	15	10	20	30	10	850
076	--	5	0	--	30	--	--	45	30	925
Simultaneous n and p drive - furnace mouth cool 120 min										
077	--	5	0	--	30	--	--	45	30	925
Simultaneous n and p drive - furnace mouth cool 120 min										

TABLE 1. PROCESSING PARAMETERS FOR POCl_3 DIFFUSION (Continued)

Lot No.	POCl ₃ (°C)	N ₂ (CFH)	O ₂ (CFH)	POCl ₃ Carrier O ₂ (CFH)	POCl ₃					
					Push (min)	Warm (min)	Deposit (min)	Drive (min)	Pull (min)	Temp (°C)
078	25	5	.02	.5	15	10	20	30	15	805
079	25	5	.5	.5	15	10	20	30	15	794
080	25	5	.5	.5	15	10	30	30	15	794
081	25	5	.5	.5	15	10	40	30	15	794
082	25	5	.05	.5	15	10	40	20	15	794
083	45	5	.5	.5	10	10	30	60	10	794
084	45	5	.05	.5	15	10	30	60	15	794
085	Room	.5	.05	.05	10	10	40	90	10	854
				N ₂ Carrier						
086	Room	4.5	1.0	.5	10	10	40	90	10	850
				N ₂ Carrier						
087	27	5	.5	.5	10	10	20	30	10	850
088	27	5	.5	.5	10	10	20	30	10	850
090	Room	4.5	1.0	.5	10	10	20	30	10	850
				N ₂ Carrier						
091	Room	4.5	1.0	.5	10	10	20	30	10	850
				N ₂ Carrier						
092	Room	4.5	1.0	.5	10	10	20	30	10	850
				N ₂ Carrier						
093	40	5	.5	.5	10	10	20	30	10	850
094	45	5	.5	.5	10	10	20	30	10	850
095	45	5	.5	.5	10	10	20	30	10	850
096	35	5	.5	.5	10	10	20	30	10	850
097	30	5	.5	.5	10	5	20	30	10	850
098	45	5	.5	.5	10	10	20	30	10	850
099	45	5	.5	.5	10	10	20	30	10	850
100	46	5	.5	.5	10	10	20	30	10	850
101	45	5	.5	.5	10	10	20	30	10	850
103	45	5	.5	.5	10	10	20	30	10	850
104	45	5	.5	.5	10	10	20	30	10	850
107	45	5	.5	.5	10	10	20	63	10	850

TABLE 2. EMISSION SPECTROGRAPHIC ANALYSES OF THICK-FILM
CATION CONSTITUENTS (ppm by weight)

Ele- ment	Engelhard				Thick Film Systems	
	E-422-C Ag	E-422-D Ag/Al	E-422-E Ag	E-422-F Ag/Al	A-250 Ag	3347 Ag
Ag	S*	S*	S*	S*	S*	S*
Al	15-150	3000-30,000	10-100	3000-30,000	10-100	20-200
Zn	100-1000	100-1000	----	30-300	30-300	30-300
Na	10-100	10-100	60-600	100-1000	15-150	20-200
Cu	20-200	20-200	200-2000	200-2000	60-600	100-1000
Fe	15-150	100-1000	10-100	100-1000	10-100	15-150
Pb	3000-30,000	3000-30,000	600-6000	2000-20,000	15-150	3000-30,000
Mg	0.6-6	30-300	20-200	60-600	30-300	6-60
Mn	0.3-3	6-60	0.3-3	10-100	1-10	1-10
Sb	30-300	30-300	----	----	----	----
Si	300-3000	500-5000	500-5000	600-6000	150-1500	600-6000
B	600-6000	600-6000	300-3000	300-3000	----	300-3000
Ba	----	10-100	----	----	----	----
Ti	----	60-600	30-300	150-1500	3-30	3-30
Ga	----	10-100	----	10-100	----	----
Cd	----	----	10-1000	100-10000	----	----
Pd	----	----	----	----	----	6-60
Bi	----	----	----	----	----	10-100
Au	----	----	----	----	----	10-100

S* = amount present is substantially above analytical range.

Two lots of 0I-6105 Ag have been analyzed and, as seen in Table 3, differ in phosphorous level by as much as 50%. This difference may or may not be significant in terms of changes in contact resistance and cell performance in general.

TABLE 3. EMISSION SPECTROGRAPHIC ANALYSIS OF
THICK-FILM CATION CONSTITUENTS
(ppm by weight)

<u>Element</u>	0I-6105 Ag	
	<u>Lot T-70526</u>	<u>Lot 71114</u>
Ag	S*	S*
P	1000-10,000	1500-15,000
Na	100-1000	100-1000
Zn	10-100	-----
Cu	100-1000	60-600
Ti	3-30	3-30
Al	15-150	60-600
Bi	1-10	1-10
Fe	6-60	2-20
Si	60-600	15-150
Pb	3-30	30-300
Mg	5-50	3-30
Mn	1-10	-----
Au	3-30	-----
Ca	-----	6-60

S* = amount present is substantially above analytical range.

2. Ink Synthesis - RCA

The raw materials for ink formulation have been acquired, prepared and analyzed as necessary. Three commercial Ag powders were selected, based on variation in particle size, and were analyzed for impurities by emission spectroscopy as shown in Table 4. Of those impurities found, Cu would most seriously affect the electrical conductivity of Ag, since 0.1 to 0.2 wt pct Cu is soluble near room temperature. The Metz* K-150 Ag perhaps exceeds this amount, but it was kept for comparative testing anyway.

Cellulosic polymers, which are used to control viscosity and green strength in the ink were also analyzed as shown in Table 5. Although the Na level is significantly above background in each case, the total quantity remaining available for diffusion into silicon is negligible when the ultimate dilution with other ink ingredients is considered.

Three specific frits or adhesive agents were prepared, two by standard glass melting techniques and ball-mill grinding. The third, AgPO_3 , was formed by chemical precipitation from the reaction between AgNO_3 and stabilized HPO_3 . The stability of the third frit is in question, since x-ray diffraction analysis identified $\text{Ag}_4\text{P}_2\text{O}_7$ and/or Ag_3PO_4 in various instances. A summary of frit properties is presented in Table 6. The good wetting exhibited by the AgPO_3 and $80\text{PbO}-10\text{B}_2\text{O}_3-10\text{SiO}_2$ frit make them excellent candidates for metallization on n- and p-type silicon surfaces, respectively.

3. Ink-Electrical Conductivity

The frit and Ag powder were incorporated into an ink vehicle consisting of 6 wt pct ethyl cellulose (N-300) dissolved in butyl Carbitol,** i.e., diethylene glycol monobutyl ether. The final solids content of the ink varied with the specific surface area of the Ag powder. The solids content of the Metz K-150 Ag could only achieve a maximum of 70 wt pct and still provide adequate screen-printing quality whereas the lower surface area powders, Metz FS type C and U.S. Metal Refining*** Lot 71-2, could be increased to 80 wt pct and still print well.

*Metz Metallurgical Company, South Plainfield, NJ.

**Carbitol is registered trademark of Union Carbide Corp., New York, NY.

***U.S. Metal Refining Co., Carteret, NJ.

TABLE 4. EMISSION SPECTROGRAPHIC ANALYSIS OF SILVER
POWDER CATION CONSTITUENTS (ppm by weight)

<u>Element</u>	<u>Metz K-150</u>	<u>Metz FS Type C</u>	<u>U.S. Metal Refining Lot 71-2</u>
Si	100-1000	50-500	60-600
Mg	2-20	5-50	10-100
Pb	10-100	6-60	15-150
Fe	2-20	3-30	10-100
Cu	600-6000	10-100	100-1000
Zn	30-300	30-300	30-300
Al	----	2-20	6-60
Ca	----	15-150	3-30
Na	----	60-600	60-600
Mn	----	----	1-10
Sn	----	----	3-30
Maximum Impurities			
Total, wt pct	0.74	0.18	0.30
Ag, wt pct	99.26	99.82	99.70
Specific Surface Area (BET Method) m ² /gm	3.4	0.88	0.24

TABLE 5. EMISSION SPECTROGRAPHIC ANALYSES OF CELLULOSIC
POLYMERS CATION CONSTITUENTS (ppm by weight)

<u>Element</u>	<u>Ethyl Cellulose*</u>	<u>Klucel**</u>	<u>Klucel</u>
	N-300	L	H
Ni	3-30	-----	-----
Na	300-3000	300-3000	60-600
Cu	6-60	150-1500	2-20
Ca	100-1000	-----	100-1000
Fe	10-100	2-20	0.6-6
Mg	5-50	5-50	5-50
Si	3-30	6-60	30-300
Ag	-----	0.03-0.3	0.6-6
Al	-----	3-30	2-20
Sn	-----	6-60	-----
Pb	-----	-----	3-30
Maximum Impurities			
Total, wt pct	0.43	0.47	0.20

*Hercules, Inc, Wilmington, DE.

**Hercules, Inc, Wilmington, DE - Klucel is registered trademark for
hydroxypropyl cellulose.

TABLE 6. FRIT PROPERTIES

Frit (wt pct)	Specific Surface Area (m ² /g)	Density (g/cm ³)	Contact Angle*	
			on Si	on Ag
PbO(80)-B ₂ O ₃ (10)-SiO ₂ (10)	0.4453	6.376	5°	14°
PbO(70)-ZnO(10)-B ₂ O ₃ (10)-SiO ₂ (10)	0.5240	6.079	36°	43°
AgPO ₃	-----	-----	18°	0

*Contact angle: after 10 min at 675°C

The test inks were screen printed through an 1874-square-serpentine line pattern (0.015 in. wide, 0.015 in. spacing) onto a 1 x 1 in. 95% alumina test substrate to determine ink conductivity. As shown in Fig. 6, the sheet resistance does not appear to vary significantly when the ink is fired for various time and temperature combinations. After microscopic measurement of the fired film thickness and computation of resistivity, the effect of increasing sintering time and temperature become more apparent, as shown in Fig. 7. However, it became obvious that determining minute differences in electrical conductivity would require a more accurate measure of metal deposited. Consequently, after sintering the test patterns, the Ag ink and substrate were weighed, the electrical resistance was measured, the Ag ink was stripped in HNO₃ and the substrate was reweighed. Hence, the exact weight of Ag deposited was obtained and this value used to compute the ideal resistance for that amount of Ag. From the observed-to-ideal resistance ratio, the percent of bulk electrical conductivity was computed and these values are reported for the RCA-formulated and commercial inks in Tables 7, 8, and 9. It should be noted that each test pattern was heated to 500°C for 2 min prior to heating to the listed combination in the tables. The one exception is shown in Table 9 where the Thick Film Systems 3347 Ag was fired at 300 and 400°C to illustrate the poor electrical conductivity achieved at these low temperatures.

Figure 6. Firing time-temperature dependence on sheet resistance of screen-printed Metz K-150 silver ink.

Figure 7. Firing time-temperature dependence of resistivity of screen-printed Metz K-150 silver ink.

TABLE 7. PERCENT OF BULK ELECTRICAL CONDUCTIVITY OF
RCA Ag INKS (NO FRIT)

<u>Time (s)</u>	<u>Temperature (°C)</u>				
	<u>500</u>	<u>600</u>	<u>700</u>	<u>800</u>	<u>900</u>
RCA - Metz K-150 Ag					
30	50	46	52	47	52
60	47	49	54	52	55
90	45	49	59	55	55
120	47	50	59	47	55
600	52	55	64	57	58
2400	49	61	69	58	58
RCA - Metz FS Type C Ag					
30	30	38	45	47	60
60	32	36	51	60	64
90	34	38	53	60	69
120	35	43	53	60	69
600	39	47	60	68	72
2400	41	53	61	70	75
RCA - U.S. Metal Refining Lot 71-2 Ag					
30	25	26	31	--	41
60	24	26	32	33	45
90	26	28	35	35	44
120	26	29	35	35	22
600	28	30	43	37	35
2400	28	36	45	25	--

TABLE 8. PERCENT OF BULK ELECTRICAL CONDUCTIVITY OF
RCA - METZ Ag vs FRIT CONTENT

<u>Time (s)</u>	<u>Temperature (°C)</u>				
	<u>500</u>	<u>600</u>	<u>700</u>	<u>800</u>	<u>900</u>
RCA - Metz K-150 Ag (no frit)					
30	50	46	52	47	52
60	47	49	54	52	55
90	45	49	59	55	55
120	47	50	59	47	55
600	52	55	64	57	58
2400	49	61	69	58	58
RCA - Metz K-150 Ag + 5 vol pct glass (80PbO-10B ₂ O ₃ -10SiO ₂)					
30	48	47	56	60	60
60	48	48	58	59	58
90	47	55	58	59	56
120	45	56	59	63	57
600	49	51	59	62	61
2400	49	53	59	66	63
RCA - Metz K-150 Ag + 10 vol pct glass (80PbO-10B ₂ O ₃ -10SiO ₂)					
30	56	58	62	69	67
60	54	59	63	70	72
90	55	62	68	74	71
120	57	61	67	71	71
600	58	64	74	75	74
2400	58	70	71	74	69

TABLE 8. PERCENT OF BULK ELECTRICAL CONDUCTIVITY OF
RCA - METZ Ag vs FRIT CONTENT (Continued)

Temperature (°C)					
<u>Time (s)</u>	<u>500</u>	<u>600</u>	<u>700</u>	<u>800</u>	<u>900</u>
RCA - Metz K-150 Ag + 5 vol pct AgPO ₃					
30	41	36	50	55	60
60	36	41	48	56	60
90	38	44	53	63	63
120	38	46	54	64	64
600	39	46	62	69	65
2400	41	50	63	67	67
<u>Time (s)</u>	<u>500</u>	<u>600</u>	<u>675</u>		
RCA - Metz FS Type C Ag + 10 vol pct glass (80PbO-10B ₂ O ₃ -10SiO ₂)					
60	25	40	45		
90	32	44	48		
120	35	45	51		
600	42	54	61		
RCA - Metz FS Type C Ag + 3 wt pct Al + 10 vol pct glass (80PbO-10B ₂ O ₃ -10SiO ₂)					
60	24	35	40		
90	27	48	39		
120	32	40	39		
600	38	48	44		

TABLE 9. PERCENT OF BULK ELECTRICAL CONDUCTIVITY OF
COMMERCIAL INKS

<u>Time (s)</u>	Temperature (°C)				
	<u>300</u>	<u>400</u>	<u>500</u>	<u>600</u>	<u>700</u>
Thick Film Systems 3347 (Ag)					
30	15	18	44	51	59
60	15	18	47	55	64
90	15	18	47	58	67
120	15	18	48	60	68
600	15	19	53	68	75
<u>Time (s)</u>	<u>500</u>	<u>600</u>	<u>700</u>	<u>800</u>	<u>900</u>
Owens-Illinois 6105 (Ag)					
30	54	61	61	65	74
60	54	56	68	71	80
90	53	55	70	75	83
120	50	56	72	79	87
600	50	62	79	87	95
2400	52	67	81	93	98
Thick Film Systems A-250 (no glass) (Ag)					
30	39	53	64		
60	42	61	70		
90	43	64	72		
120	44	67	74		
600	51	73	80		
Englehard E-422-C (Ag)					
30	55	57	63		
60	56	61	66		
90	57	62	69		
120	58	62	70		
600	61	70	76		

TABLE 9. PERCENT OF BULK ELECTRICAL CONDUCTIVITY OF
COMMERCIAL INKS (Continued)

<u>Time (s)</u>	Temperature (°C)				
	<u>500</u>	<u>600</u>	<u>700</u>	<u>800</u>	<u>900</u>
Engelhard E-422-E (Ag)					
30	42	45	49		
60	42	47	53		
90	43	48	55		
120	43	48	57		
600	46	52	62		
Engelhard E-422-D (Ag/Al)					
30	42	44	36		
60	42	45	33		
90	44	45	32		
120	44	46	33		
600	46	47	32		
Engelhard E-422-F (Ag/Al)					
30	35	37	22		
60	35	38	9		
90	35	38	9		
120	36	39	9		
600	38	39	7		

In Table 7, which compares the unfritted RCA-formulated Ag inks, the highest conductivities are achieved by the Metz K-150 ($3.4 \text{ m}^2/\text{g}$ surface area) and Metz FS Type ($0.88 \text{ m}^2/\text{g}$). The values for the 600 to 700°C regime range from 47 to 64% of bulk electrical conductivity when fired for 600 s. However, the U.S. Metal Refining Ag ($0.24 \text{ m}^2/\text{g}$) only achieved 30 to 43% under the same conditions. The latter Ag powder is therefore excluded from further testing.

In Table 8 the influence of various frit additions upon electrical conductivity of Metz K-150 and FS Type C silver is compared. It can be seen that the presence of sufficient frit, i.e., 10 vol pct, improves conductivity as predicted by liquid-phase-assisted sintering theory [2]. For example, at the 600-s firing time, the percent of bulk electrical conductivity increases from 55 to 64 when fired at 600°C and 64 to 74 when fired at 700°C for the Metz K-150 Ag. The percent of bulk electrical conductivity for Metz FS Type C with 10 vol pct frit fired at 600°C-600 s, however, is only equivalent to the pure, unfritted Metz K-150. This result is also expected, since larger Ag particles in the FS Type C powder do not sinter as rapidly as the smaller particles in the K-150 powder.

Despite the lower electrical conductivity of the FS Type C powder, a greater solids content in the ink is possible due to the lower surface area of the Ag, i.e., 80 wt pct vs 70 wt pct for the K-150. This difference showed up in the fired film appearance which was more dense than the K-150 Ag film, and may influence solderability and adhesion properties.

The one test completed with 5 vol pct addition of AgPO_3 showed lower conductivity (Table 8) than pure K-150 Ag when fired at 500 to 700°C. At 800 to 900°C the conductivity of the AgPO_3 based ink was greater than the pure K-150. This improvement at the higher temperatures implies that the AgPO_3 precipitate was not pure but contained higher melting compounds, e.g., $\text{Ag}_4\text{P}_2\text{O}_7$ (m.p.* 585°C) and Ag_3PO_4 (m.p. 849°C) vs AgPO_3 (m.p. 482°C). Thus the benefit derived from liquid-phase sintering did not occur until these compounds melted. Further development is needed with AgPO_3 stabilization to improve the desired effect of low temperature liquid-phase-assisted sintering.

For contact to the p-type Si on the back of the cell, a Ag + 3 wt pct Al ink was prepared containing 10 vol pct glass. As shown in Table 8, the

2. K. R. Bube and T. T. Hitch, "Basic Adhesion Mechanisms in Thick and Thin Films," Final Report, March 1978, NASC Contract N00019-77-C-0176.

*m.p. = melting point.

conductivity is generally lower than the unalloyed Ag inks for equivalent firing conditions. In air firing, two competing reactions are occurring, namely, oxidation of the Al powder and alloying with the Ag. Both tend to reduce the electrical conductivity, while sintering tends to raise it. Extended time at higher temperature appears to have a neutral to negative effect upon conductivity.

The electrical conductivity of commercial inks appears in Table 9 and shows data for Thick Film Systems 3347, A-250, Owens-Illinois 6105, Engelhard E-422-C, E-422-E, E-422-D (Ag/Al), and E-422-F (Ag/Al). When fired at 300 to 400°C the TFS 3347 Ag never exceeds 19% of bulk electrical conductivity, indicating the basic reason for much higher peak firing temperatures. When fired at higher temperatures, the conductivities are slightly higher than the RCA-Metz K-150 with 10 vol pct glass. Without careful analysis of Ag particle size distribution and glass composition and content, it is difficult to surmise which, if not all, factors are contributing to the improvement. When TFS 3347 is compared with fritless TFS A-250, the higher electrical conductivity of the latter is also difficult to assess. At least the three previously mentioned factors can influence conductivity, i.e., Ag particle size distribution, glass content, and glass composition. For example, if the glass content is not sufficiently high or the glass viscosity is not sufficiently low at the selected firing temperatures, the conductivity will not be as high as the pure Ag ink, in keeping with liquid-phase-assisted sintering.

The phosphorus-bearing OI-6105 Ag shows progressively superior conductivity with increasing temperature when compared with RCA-Metz K-150 in the 700 to 900°C range. It is the only ink which actually approaches pure Ag conductivity when fired at 900°C for 2400 s. However, in the region of interest, e.g., 600 s at 600 to 700°C, the inks are about equal in conductivity.

Limited testing was also completed on two Engelhard Ag and two Engelhard Ag/Al inks. One Ag ink, E-422-C, shows slightly superior conductivity in the 600 s, 600 to 700°C region and the other, E-422-E, considerably lower conductivity than the RCA-Metz K-150 ink. Similarly, the Ag/Al inks are about comparable or slightly lower in conductivity.

In addition to Ag inks, a Cu ink, Cermalloy* 7029-5, was analyzed as shown in Table 10 and found to contain a lead borosilicate frit, similar to the

*Division of Bala Electronics, West Conshohocken, PA.

Table 10. EMISSION SPECTROGRAPHIC ANALYSIS OF THICK-FILM CATION CONSTITUENTS (ppm by weight)

<u>Element</u>	<u>Cermalloy Cu 7029-5</u>
Cu	S*
Ni	1-10
Pd	150-1500
Ag	10-100
Na	60-600
Zn	20-200
Ca	10-100
Al	150-1500
Bi	0.6-6
Fe	6-60
Si	200-2000
Pb	1000-10000
Mg	6-60
Mn	50-500
B	300-3000

*S = amount present is substantially above analytical range.

Ag inks. Conductivity data for the Cu ink was obtained after firing in tank N₂ and deoxidized tank N₂ and, as shown in Table 11, is considerably lower in conductivity in the area of interest, e.g., 600 to 700°C, than the RCA-Metz K-150 Ag ink.

Furthermore the dot-to-dot pattern, used for determining specific contact resistance, was applied to a silicon solar cell (lot 85). The contact resistance was measured after firing at 500, 600 and 700°C, respectively, for 5 min and found to be 1.77 $\Omega\text{-cm}^2$ at 500°C, 0.70 $\Omega\text{-cm}^2$ at 600°C and 0.41 $\Omega\text{-cm}^2$ at 700°C. The combination of high contact resistance and low electrical conductivity for the Cu ink is not encouraging. Therefore, attention will continue to be directed toward the Ag inks.

TABLE 11. PERCENT OF BULK ELECTRICAL CONDUCTIVITY

Cermalloy 7029-5 (Cu)					
Time (s)	Temperature (°C)				
	500	600	700	800	900
Ambient: Tank N ₂ , preheat 500°C-2-min					
30	22	27	33	41	45
60	22	28	40	48	55
90	22	36	43	51	57
120	24	33	46	50	56
600	28	48	54	59	62
2400	28	53	61	57	--
Ambient: Deoxidized N ₂ , without 500°C-2-min preheat					
60	4	24	35	43	55
90	9	28	40	50	58
120	12	31	50	53	61
600	19	44	53	62	71

4. Laser Heating of Screen-Printed Line

To test the effectiveness of laser heating as a quick means of sintering a screen-printed Ag line, a small comparative test was carried out. A 0.015-in.-wide x 0.75-in.-long test bar was screen-printed onto single-crystal Si pieces. Samples A and B were preheated after printing to burn out the polymer in the ink at 400°C for 30 s. If the ink polymer is not removed prior to exposure to the laser beam, the pattern is explosively removed upon laser pulsing.

Sample A was exposed to a Nd:glass laser pulse of 2.9 J/cm^2 and a second pulse of 3.6 J/cm^2 . Sample B was fired in a belt furnace set to achieve about a 10-min dwell at 675°C. Electrical measurement showed sample A (laser pulsed) decreased in electrical resistance about 13% while sample B decreased about 58%. This limited experience is not encouraging for rapidly sintering a screen-printed Ag line on Si.

5. Screen-Printing Parameters

To check the possibility of a silicon wafer cracking during or following screen printing, a worst-case printing test was devised. It is known that screen-printing variables, e.g., squeegee speed, snap-off distance (screen-to-substrate distance), and squeegee compression can affect the uniformity of ink deposited. For example, Fig. 8 illustrates the change in coefficient of variation of ink weight deposited as a function of the three key variables. Normal printing is done in a squeegee speed range of 3 to 6 in./s and a snap-off distance of 0.025 to 0.040 in. Squeegee compression, which directly affects the force applied to the substrate to be printed, is best kept within the 0.006- to 0.012-in. range. Excessive squeegee compression, although useful in improving deposited-ink uniformity, unnecessarily stresses the substrate and hastens squeegee wear.

The applied force vs squeegee compression was measured directly with a force gage and found to be about 0.6 lb at 0.009-in. squeegee compression as shown in Fig. 9. This midrange compression value was then used for the test. Nine silicon wafers, as-sawed, and measuring about 0.022 in. thick were screen printed with the collector grid pattern on both sides of the wafer at 90° orientation to each other. This orientation maximized the stress applied to the wafers midway between the collector grid lines. The printed wafers were cleaned to remove the dried ink deposit and, along with an unprinted control wafer, exposed to a thermal shock cycle. The wafers were immersed in liquid N₂ (-196°C) for 20 s and transferred rapidly to liquid 1-octodecanol (200°C), held there for 20 s, and transferred rapidly to liquid methanol (45°C) to remove the 1-octodecanol. This cycle was repeated five times for all wafers. All wafers were subsequently examined microscopically and after etching* to delineate any cracks which may have formed during printing, thermal shocking, or etching. No cracks were found. It is therefore assumed that normal screen-printing forces will not damage wafers containing stress-raising flaws induced by the sawing operations.

*50cc HNO₃, 30 cc HF, and 30 cc acetic acid.

Figure 8. Effect of coefficient of variation of various screen-printing parameters.

Figure 9. Applied force as a function of squeegee compression in screen printing.

6. Solar-Cell Metallization Diagnostics

In Table 12, the solar-cell characteristics of five lots of solar cells with evaporated metal contacts are listed as well as the screen-printed samples from lot 047. The collector grid was screen printed with OI-6105 Ag, fired at 500°C for 2 min plus 675°C for 10 min. Subsequently Al metal was evaporated on the back of the cells and diffused in at 480°C.

One can surmise from Table 12 that there is a statistically insignificant difference in the cell characteristics when comparing evaporated metal and screen-printed cells. When screen printing was applied to lot 060, which showed average cell performance with evaporated metal contacts, the cell output was nil.

Samples of screen-printed wafers from lots 047 and 060 were analyzed for surface concentrations of P and Ag, as shown in Table 13, by electron-probe microanalysis. Measurements were taken on the as-fired Ag lines, in-between the lines (on the n-Si surface) and on the phosphate-frit region of the Ag line after removal of the Ag by dissolution in $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$.

A comparison of relative phosphorus concentration on the surface of the Ag lines indicates that a much greater amount is present in lot 060, which

TABLE 12. SOLAR-CELL CHARACTERISTICS EVAPORATED
METAL CONTROL vs SCREEN-PRINTED METAL

Lot No.	Contacts									
	Evaporated Metal					Screen-Printed Metal				
	η^*	J_{sc}	V_{oc}	F.F.		η	J_{sc}	V_{oc}	F.F.	
047	$\bar{x}$	6.32	18.88	0.54	0.61	$\bar{x}$	6.53	17.13	0.55	0.67
	σ	0.79	1.31	4.5×10^{-3}	0.06	σ	1.01	1.09	5.3×10^{-3}	0.08
	n	5	5	5	5	n	7	7	7	7
	%V	12.6	6.9	0.8	11.0	%V	15.5	6.4	0.96	12.3
057	$\bar{x}$	7.60	18.16	0.55	0.74					
	σ	1.08	2.04	0.02	0.01					
	n	4	4	4	4					
	%V	14.3	11.2	3.8	1.7					
059	$\bar{x}$	7.19	17.83	0.54	0.72					
	σ	1.24	2.05	0.02	0.02					
	n	4	4	4	4					
	%V	17.2	11.5	4.0	2.5					
060	$\bar{x}$	6.71	19.00	0.54	0.63					
	σ	1.39	1.44	0.01	0.11					
	n	5	5	5	5					
	%V	20.7	7.6	2.6	17.2					
066	$\bar{x}$	5.92	16.01	0.52	0.69					
	σ	0.64	1.88	0.02	0.04					
	n	10	10	10	10					
	%V	10.9	11.7	3.8	6.0					
5 Lots	$\bar{x}$	6.75	17.98	0.54	0.68					
	%V	9.9	6.7	2.0	8.3					

*No AR coating

TABLE 13. ELECTRON-PROBE MICROANALYSIS OF AG-INK LINES ON SOLAR-CELL WAFERS

X-ray spectral-line net intensity counts/30 s					
<u>Lot</u>	<u>Sample</u>		<u>Pkσ</u>	<u>AgLσ1</u>	
47	Ag ink	$\bar{x}$	7937	160445	
		σ	1152	3686	
		n	3	3	
	Ag removed	$\bar{x}$	22950	2188	
		σ	1176	69	
		n	3	3	
	Between lines		1491	444	
	60	Ag ink	$\bar{x}$	19289	157781
			σ	1789	4244
n			3	3	
Ag ink removed		$\bar{x}$	14915	16853	
		σ	464	407	
		n	3	3	
Between lines		746	1408		

failed to perform well electrically, than in lot 047 which did perform well. When Ag is removed from the lines, the relative concentrations of phosphorus are reversed, a greater concentration of phosphorus is present in the residual frit which is in contact with the n-Si layer in lot 047 than in lot 060. However, in both lots the surface concentrations of phosphorus, after Ag removal, are much greater than those present before removal. Since it is not known how much additional phosphorus is necessary to provide improved contact to the n-Si layer, it cannot be conclusively stated that the differing relative amounts are significant in terms of lowering specific contact resistance.

Note that one other difference in Table 13, the acceptable lot 047 n-Si phosphorus concentration, i.e., between the Ag lines, is approximately three times greater than the concentration in the electrically deficient lot 060 n-Si. Although some measurement error may be present, note the abnormally

high Ag concentration between the lines in lot 060, the phosphorus concentration difference implies a greater doping was present in the electrically acceptable lot 047. Since the analytical technique detects surface as well as some sub-surface phosphorus, one cannot categorically claim that lot 047 and lot 060 *surface* doping is different by a factor of three. However, the test results do imply that screen-printed contacts are more sensitive to variations in surface doping than evaporated metal contacts.

Further cell measurements on wafers with variable doping levels are needed to clarify this critical point. Secondary ion mass spectroscopy (SIMS) will be used to help distinguish phosphorus concentration profiles more clearly in comparing cell performance with evaporated metal and screen-printed contacts.

C. AR COATING

1. AR Coating Materials Parameters for Spray Solution System

Deposition of a mixed $\text{SiO}_2\text{-TiO}_2$ coating by spinning and baking of a proprietary solution of an ethanol-diluted organometallic compound mixture has previously led to good optical antireflection results on planar silicon substrates. However, this process is not suitable for high-speed, low-cost mass production, and can lead to problems of shadowing and nonuniformities if cells with thick metallization grids are to be coated. On the basis of the satisfactory optical qualities we decided to utilize the basic starting material, but to modify and optimize a solution system for spray application. We are aiming at a uniform layer in the 600- to 800-Å thickness range with a refractive index of 2.0 to 2.2. The exact optimal properties will be determined from experimental results.

The following parameters must be considered in formulating a successful solution system for spray application: component solubility characteristics, miscibility, rate of evaporation, surface wettability, flow properties, viscosity, degree of hydrogen bonding and dielectric constant of solution components, chemical reactivity, cost, toxicity, and long-range stability. The solution to be sprayed must have a viscosity compatible with the available orifice sizes of the spray nozzle and the pressure range of the equipment. Both viscosity and surface tension must be such that the sprayed-on micro-droplets will spread locally on the substrate surface and coalesce, forming

a thin homogeneous liquid film of uniform thickness. Spreading must not be excessive to avoid build-up or depletion along the periphery of the cell. The final coating must have good adhesion and integrity, be reasonably uniform in thickness over the entire cell surface, be free of haze and gross structural imperfections, and, above all, exhibit on silicon substrates minimum reflectance and absorbance in the visible wavelength midregion. Except for the optical properties, which are primarily determined by the $\text{TiO}_2/\text{SiO}_2$ ratio, the properties noted are functions of the solution components. The exact film thickness is readily adjustable by selecting proper settings (such as travel speed) on the spray equipment system.

We therefore decided to first test the effects of numerous organic solvents by diluting 1 volume of the proprietary titania-silica concentrate with 1 to 3 volumes of a solvent ("primary solvent"). Smaller volumes of a second solvent ("secondary solvent") were added in most cases, and dilution ratios were varied within each system. A list of the solvent tested is presented in Table 14. A great many solvent combinations were eliminated at once on the basis of incompatibility with the reagent, as manifested by solution immiscibility, color or gel formation, turbidity, cloudiness, precipitation, separation of components during drying of the liquid film, and haze or crystallite formation in the resulting solid coating. Other disqualifying properties include excessively slow or fast evaporation of a component solvent and nonuniform spreading. These initial tests were made by standardized manual spraying and shake-out treatments. The surviving 11 systems that showed promise are underlined in Table 14 and were next investigated by spraying in a Zicon* machine under controlled conditions. Nine of these potentially successful systems contain 2-ethyl-1-hexanol as one of the solvent components, with ethanol, isopropanol, sec-butanol, ethyl acetate, or methyl ethyl ketone as the other component. The key spray solution component is clearly 2-ethyl-1-hexanol.

A summary of the results from the Zicon spray tests with these 11 solution systems in terms of film-forming quality is presented in Table 15. Except for equipment adjustments to produce film thickness in the 600- to 800-Å range (after drying and baking), spraying was performed under standardized conditions

*Zicon Corporation, Mount Vernon, NY.

TABLE 14. SOLVENT SYSTEMS EVALUATED FOR TITANIA-SILICA
AR SPRAY COATINGS

Solvent Group	Primary Solvent	Secondary Solvent	Solution System*
alcohols	ethanol	-----	
	ethanol	2-ethyl-1-hexanol	
	isopropanol	-----	
	isopropanol	Cellosolve** acetate	
	isopropanol	2-ethyl-1-hexanol	
	sec-butanol	-----	
	sec-butanol	2-ethyl-1-hexanol	
	sec-butanol	iso-amyl alcohol	
	sec-butanol	ethyl acetate	
	iso-amyl alcohol	-----	
	iso-amyl alcohol	2-ethyl-1-hexanol	
	iso-amyl alcohol	ethyl acetate	
	<u>2-ethyl-1-hexanol</u> --	-----	D
	<u>2-ethyl-1-hexanol</u> --	<u>ethanol</u> -----	G, K
	<u>2-ethyl-1-hexanol</u> --	<u>isopropanol</u> -----	L
	<u>2-ethyl-1-hexanol</u> --	<u>sec-butanol</u> -----	E
	<u>2-ethyl-1-hexanol</u> --	<u>ethyl acetate</u> -----	F
	<u>2-ethyl-1-hexanol</u> --	<u>methyl ethyl ketone</u> --	B, J
esters	ethyl acetate	-----	
	ethyl acetate	2-ethyl-1-hexanol	
	ethyl acetate	isopropanol	
	butyl acetate	-----	
	butyl acetate	ethanol	
	butyl acetate	Cellosolve** acetate	
	<u>butyl acetate</u> --	<u>2-ethyl-1-hexanol</u> --	C
	amyl acetate	-----	
	Cellosolve** acetate	-----	
	<u>Cellosolve** acetate</u> --	<u>iso-amyl alcohol</u> -----	A
	amyl acetate	-----	
	Cellosolve** acetate	-----	

TABLE 14. SOLVENT SYSTEMS EVALUATED FOR TITANIA-SILICA
AR SPRAY COATINGS (Continued)

Solvent Groups	Primary Solvent	Secondary Solvent	Solution System [*]
esters (cont.)	2-methoxyethyl acetate	-----	
	2-ethoxyethyl acetate	-----	
	2-butoxyethoxy ethyl acetate	-----	
	2, (2 ethoxyethoxy) ethyl acetate	-----	
	ethyl acetate	-----	
	2, (butoxyethyl) ethyl acetate	-----	
ketones	acetone	-----	I
	methyl ethyl ketone	-----	
	<u>diacetone alcohol</u> _ _	-----	
hydrocarbons	hexane	-----	
	cyclohexane	-----	
	toluene	-----	
	xylene	-----	
chlorohydrocarbons	methylene chloride	-----	
	1,2-dichloro ethane	-----	
others	dimethyl sulfoxide		

Note:

*Refer to Table 15.

**Cellosolve is ethylene glycol monoethyl ether; Union Carbide trade name.

Underlining indicates initially promising systems investigated further by Zicon spray testing (see Table 15).

TABLE 15. SUMMARY OF RESULTS FROM ZICON SPRAY TESTS FOR AR COATING

Solution System	Constituents: (2) 1 vol Concentrate (3) +	Physical Film Qualities, Grading (4)				Quality Index	Remarks	Best Overall Systems
		Flow Prop- erties	Micro Tex- ture	Gel, Partic- les	Thickness Unifor- mity			
A	1 vol iso-amyl alcohol + 2 vol cellosolve acetate	2	3	2	3	10	useless for spraying applications	
B	1 vol 2-ethyl-1-hexanol + 1 vol methyl isobutyl ketone	2	2	3	1	8	particle density increases with spray time	
C	1 vol 2-ethyl-1-hexanol + 1 vol butyl acetate	2	2	3	1	8		
D	2 vol 2-ethyl-1-hexanol	1-	1	3	1	6-		
E	1 vol 2-ethyl-1-hexanol + 1 vol sec-butanol	2	2	2	1	7		X
F	1 vol 2-ethyl-1-hexanol + 1 vol ethyl acetate	1	2	3	1	7	particle density decreases with spray time	
G	0.5 vol ethanol + 1.5 vol 2-ethyl-1-hexanol	2	2	2	1	7		X
I	2 vol diacetone alcohol	2	2	3	2	9	useless for spraying applications	
J	0.2 vol ethanol + 1 vol 2-ethyl-1-hexanol + 1 vol methyl ethyl ketone	2	2	3	1	7		
K	1 vol ethanol + 1 vol 2-ethyl-1-hexanol	2	2	3	1	8	small-grain particulates only	
L	1 vol isopropanol + 1 vol 2-ethyl-1-hexanol	2	1	2	1	6	small-grain particulates only	X
M	1 vol ethanol, spin-on (5) for comparison	2	1	2	2	7	spin-on (6); particles cause comets	

(1) Standard Model, Zicon Series 11000 Autocater. Substrates were Si wafers and 7.5-cm diam metallized solar-cell structures.

(2) In the sequence of addition.

(3) Titania-Silica Film "C", special concentrate (Organometallic Composite) by Emulsitone Co., Whippany, NJ.

(4) Grading as follows: 1-good, 2-fair, 3-poor. Evaluation after standard, immediate post-deposition heat treatments in room air (60 s drying in IR oven at 200°C, 60 s curing at 200°C and 60 s densification at 400°C on hot plates).

(5) Titania-Silica Film "C", formulation for spin-on applications by Emulsitone Co., Whippany, NJ.

(6) Spun on at 3300 r/min, 30 s; (for comparison with spray-on deposits).

so that the resulting films were directly comparable. Three solution systems were judged outstanding from these tests: 2-ethyl-1-hexanol with either ethanol (G), isopropanol (L), or sec-butanol (E). Several of the other systems were nearly as good and were comparable to the spun-on coating (system M). All films showed consistent contamination with particles of varying density, to be discussed in subsection C.4 below.

Substrates for the spraying tests summarized in Table 15 were polished, chemically cleaned ($\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$) silicon wafers (5-cm diameter), simulated silicon solar cells (7.5-cm diameter wafers with fired metallization grid on one side), and a few completed solar cells for preliminary tests.

Addition of surfactants to improve the wetting characteristics, and of thickening agents to modify the solution viscosity, were considered but found unnecessary to achieve the desired results.

2. Variables of Spray Deposition Equipment

Preliminary tests were carried out with several of the solution systems listed in Table 15 to select the basic machine variables suitable for our purpose. Chrome-metallized glass plates were used as sensitive substrates. Subsequently, the following variables were fixed and held constant throughout the investigation:

Orifice size	0.31 mm	(0.012 in.)
Spray pressure (N_2)	172 kPa	(25 psig)
Index distance controlling substrate transport advance rate	2.54 cm	(1.0 in.)
Spray gun traverse speed	36 cm/s	(14 in./s)

Manipulated machine variables to attain the proper film thickness were:

Liquid delivery pressure	1.0 to 7.5 kPa	(4 to 30 in. H_2O)
Spray gun height above substrate	10 to 15 cm	(4 to 6 in.)

It was found that, as a first approximation, both liquid delivery pressure and spraying duration are linear control parameters in attaining a desired film thickness, whereas gun-to-substrate distance affects film thickness nonlinearly, as can be expected. Quantitative data and procedural details will be presented at a later date for the final solution system to be selected.

3. Solar-Cell Surface Conditions Before Coating

Since the creation of a uniform coating is strongly affected by the surface conditions of the substrate, different chemical types of silicon surfaces were tested with the solution systems in Table 15. Hydrophilic silicon surfaces were prepared by cleaning polished wafers with a freshly mixed 30% H_2O_2 (unstabilized) - 98% H_2SO_4 (1:1 by volume) mixture at about 100°C for 15 min to remove both organic and trace metal contaminants, followed by rinses in flowing deionized and distilled water, and terminated by spin drying. Inorganic hydrophobic silicon surfaces were prepared by dipping the wafers cleaned by the above procedure in 49% $\text{HF}-\text{H}_2\text{O}$ (1:10 by volume) for 30 s, followed by water rinsing and spin drying. Organic hydrophobic silicon surfaces were attained by spin coating the $\text{H}_2\text{O}_2-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ cleaned wafers with hexamethyl disilazane, followed by a bake out treatment at 200°C. Comparative coating tests showed no discernable differences for these three types of surfaces. Hence, we decided to conduct all coating tests with the $\text{H}_2\text{O}_2-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ cleaned surfaces, since this is the standard cleaning procedure for the cells prior to screen printing of the metallization grids. Coating tests with metallized solar-cell structures gave equivalent results, even though the surface treatment had been conducted prior to the metallization processing. However, this statement holds only for uncontaminated cells that have been kept clean under dust-free storage conditions. Particulate contaminants cause pinholes and other localized structural defects in the films, and organic contaminants (such as fingerprints) cause gross nonuniformities in the film thickness.

The metallization lines, which are typically 15 to 20 μm thick after firing, do not cause a serious problem, as tested by electrical measurements with coated cells. The AR film thickness in the immediate vicinity of the lines is thinner than in the areas between the lines, apparently due to the creation of vapor flow patterns during spray coating or liquid surface tension effects. Further improvements of this parameter are anticipated for the optimized coating process.

4. Properties of the AR Coating

Preliminary optical characterization of the spray coatings obtained from several preferred solution systems were made and compared with that obtained

by spin-on application. The measurements reported in Table 16 were taken after additional post-storage heat treatments (15 min 200°C plus 15 min 400°C in room air). Ellipsometry was used to determine film thickness and refractive index. Spectrophotometric curves of reflectance as a function of wavelength from 350 to 1000 μm were recorded, with an uncoated silicon substrate in the spectrometer reference beam. The refractive indices of the sprayed and spun-on coatings were within 3.5%; the reflectance minima vary with the thickness and can be set by any desired wavelength. The data show that the optical quality of the coatings deposited by the two techniques are very similar.

A defect common to all coatings we have prepared by both spraying or spinning is the presence of microscopic particulates which cause pinholes in the heat-treated, solid films. The density of the particles per unit area varies for different solution systems, and so does the size of the particles, as noted in Table 15. Most of the particles are crystallites and are present already in the original concentrate. Membrane filtration of the solution mixture prior to application alleviates the condition to a certain extent but requires further testing before we can arrive at optimal conditions. It is possible that these crystallites form by premature nucleated and localized hydrolysis of the organo-metallic esters that constitute the reactive silicon and titanium components of the system. However, judging from the optical measurements, this defect is no serious problem and is mainly cosmetic. Furthermore, electrical characteristics of our typical solar cells (7.5-cm diameters) spray coated with solution systems K and L (Table 15) were comparable with those of cells coated by conventional spinning, even though the sprayed cells were coated under nonoptimal conditions.

Additional optical measurements, as well as chemical and physical characterization of the films, will be made during the next and final part of the project.

5. Heat Treatment Effects

The drying and baking procedures for the liquid spray coating are critical as they affect the integrity, thickness, and refractive index of the solid AR film. Relatively gradual initial drying of the freshly deposited film in an infrared heated furnace is important; too fast a heating will disrupt the film. A 60-s treatment in the furnace appears to be sufficient. In addition, subsequent bake-out for 60 s at 200°C in room air on a hot plate, followed by

TABLE 16. TYPICAL OPTICAL PROPERTIES OF SPRAYED VS SPUN AR COATINGS
(After 15 min at 200°C and 15 min at 400°C post-storage additional heating)

Solution System ⁽¹⁾	Application of Coating	Sample No. ⁽²⁾	Interference Color	Film Thickness ⁽³⁾ (Å)	Refractive Index ⁽³⁾ (n)	Reflectance Minimum ⁽⁴⁾ (%R) (λ)		Reflectance of 5 % at λ ₁ λ ₂	
G	Zicon Spraying	10c	bluish purple	601	2.082	0.7	490	460	550
L	Zicon Spraying	2c	bluish purple	667	2.064	0.5	550	510	610
M	Centrifuge Spinning	5c	bluish purple	614	2.134	---	---	---	---
		6c	dark blue	~750	~2.1	0.2	580	530	655

Notes: (1) See Table 15 for definitions of solution systems.

(2) Coatings on polished silicon wafers that were chemically cleaned with hot H_2O_2 - H_2SO_4 - H_2O .

(3) Measurements by ellipsometry at a wavelength λ of 5461 Å.

(4) Measurements by spectrophotometry (Beckman Model DB-G, with uncoated Si substrate in reference beam; scanning from 350 to 1000 μm).

----- no measurements done .

400°C for 60 s to cure and harden the colloidal films, has been used as the standard procedure immediately following the spraying process. Additional heating at 200 and 400°C on a hot plate in room air for 15 min each, after storage of the film, decreases the film thickness further by structural densification and increases the refractive index, as seen from the results summarized in Table 17. The brief initial heat treatments appear to be sufficient for attaining an AR coating of desired properties, but additional heat treatments can be used to modify the optical film properties. Additional more detailed measurements will be conducted to correlate film properties with post-deposition heat treatments.

All work reported has been carried out at an ambient room air relative humidity level of 35%.

6. Conclusions

We have demonstrated that AR coatings can be deposited successfully onto metallized silicon solar cells by automated spraying in a Zicon series 11000 Autocoater.

An organometallic component mixture yielding SiO_2 and TiO_2 containing films on hydrolysis and heat treatment is well suited for this purpose, but is useable only in conjunction with an optimal solvent system especially designed for spraying.

The essential component of the solvent system was discovered to be 2-ethyl-1-hexanol. Secondary solvent components are less critical, and can be selected from several compounds.

Particulate crystallites form in the solution system and constitute a source of contamination which we will attempt to minimize even though the problem has been demonstrated to be basically a cosmetic one.

Preliminary measurements have indicated that the originally anticipated 30-min heat treatment of 200 and 400°C can be reduced to a duration of only 3 min, which is of considerable technical significance with respect to processing cost.

The overall electrical efficiency of typical solar cells (7.5-cm diameter, metallized by screen printing) increased by a factor of 1.4, from 7.9% before AR spray coating to 11.2% after coating, even though the spraying process has not yet been optimized.

TABLE 17. TYPICAL OPTICAL PROPERTIES OF AR COATINGS AS A FUNCTION OF HEAT TREATMENTS

Solution System(1)	Application of Coating	Sample No. (2)	Heat Treatments in Room Air	Film Thickness (A) (3)	Refractive Index (n) (3)	Reflectance Minimum(4) (%R) (λ)	Reflectance (4) of 5 % at	
							λ_1	λ_2
G	Zicon Sprayed	10a	Standard Post-Deposition(5)	693	2.034	0.5 570	520	650
		10b	Standard Post-Dep. + 15 min 200°C	---	---	0.7 560	515	635
		10c	Standard Post-Dep., +15 min 200°C, +15 min 400°C	601	2.082	0.7 490	460	550
L	Zicon Sprayed	2a	Standard Post-Deposition (5)	---	---	0.7 610	560	685
		2c	Standard Post-Dep., + 15 min 400°C	667	2.064	0.5 550	510	610
M	Centrifuge Spun	5a	Standard Post-Deposition (5)	---	---	0.8 600	540	660
		5b	Standard Post-Dep., +15 min 200°C	---	---	0.2 600	540	670
		5c	Standard Post-Dep., +15 min 200°C, + 15 min 400°C	---	---	0.2 580	530	655
		6c	Standard Post-Dep., + 15 min 200°C, + 15 min 400°C	614	2.134	---	---	---

Notes: (1) to (4) Same explanations as on Table 16.

(5) Standard post-deposition heat-treatment as defined in Table 15.

D. INTERCONNECT AND PANEL ASSEMBLY

1. Welding Evaluation

Both Ti/Ag and screen-printed silver metallizations have been investigated for suitability with parallel gap weldings as follows:

- A cell is measured for virgin I-V and P-V response, using an automatic tester. This tester uses three Sylvania ELH Lamps to uniformly illuminate the cells at 100-mW/cm^2 total energy rate. The tester varies the external load to the cell, from open-circuit to short-circuit conditions, plotting current vs voltage, and power vs voltage.
- One or more interconnect straps are welded to the cell, using a Hughes HPC-500 welder. Variables are contact pressure, weld voltage, weld duration, and electrode "footprint."
- A second I-V curve is obtained for the cell and the degradation in peak power and I-V curve shape noted. Power degradation is divided by the number of weld cycles to obtain a value per weld.
- Welded interconnects are then subjected to a peel test to failure at a 45° angle to the cell surface. Failure sites are examined to determine the quality of the weld and correlate the type of failure with the peel strength.

Approximately 100 welds have been made. For the Ti/Ag *evaporated* metallizations, several samples of OCLI* cells yielded peel strengths of 4 lb per weld (2 weld "nuggets") with peak power degradation of 1% per weld. RCA cells yield comparable values. Appropriate weld parameters are 0.55 V at 100-ms duration, 2-lb tip force on 400-psi tip pressure with tips of 0.025×0.045 in. Gap is set at 8 mil. Failure mode usually exhibits cracking of the silicon.

However, consistency of quality for a series of welds requires considerable care and attention to cleanliness of interconnect strap and electrodes, as well as contact conditions (strap and cell flatness). As the first weld cycle is made, the strap oxidizes to some extent, due to the heating. Also, some distortion occurs. As a result, the second weld cycle will generally not produce as good a nugget.

*Optical Coating Laboratories, Inc., Santa Rosa, CA, $2 \times 4 \text{ cm}^2$, space grade cells.

Screen-printed contacts have fared significantly worse than evaporated contacts. No combination of weld voltage and dwell time has been found that will result in acceptable welds. High energy content will provide bonding to the metallization, but the metallization delaminates readily from the cell. Low-energy content fails to produce bonding at all.

The tentative conclusion is therefore that welding is not a suitable assembly process for cells of current design.

2. Soldering Evaluation

For the same family of cells, the experiments were repeated using a silver-bearing solder (62% tin, 36% lead, 2% silver). Bond strength for evaporated contacts is equivalent to a welded contact. Strength for silver-screened metallization is less, but peel strength of 8 lb/in. at 45° can be obtained.

Silver-screened metallization must be soldered with some care, however, because exposure to liquid solder causes solution of the silver and consequent de-wetting of the contact between the silver/frit and the silicon. This process both degrades electrical contact and weakens the mechanical bond.

Maximum strength therefore requires minimum soldering temperature and time, consistent with good joints. Results to date have been accomplished primarily by hand soldering, with a few contacts assembled by parallel gap heating to cause solder reflow.

For production purposes, it is presently assumed that each cell will be tabbed individually with three copper interconnect strips, using a spot reflow device. (The cells and strips will have been pre-tinned and cleaned). The reflow can be done by hot air, or conduction contact with a hot plug, or by resistance heating. The cell-to-cell interconnect will then be accomplished by accumulating an entire panel set of cells in the final configuration and reflowing all of the joints by clamping the cell array between a silicone rubber pad and a hot plate.

The method of "mass soldering" of an entire array by clamping it on a hot plate has been verified on a small scale (9 cells) during this quarter, and it is intended that the technique will be demonstrated for a full 4- by 4-ft panel. A critical advantage of this process is the inherent low probability of faulty reflow joints. In fact, a joint that is of marginal quality as a result of the pretabbing operation tends to be repaired in the mass soldering operation.

3. Panel Lamination - PVB Process

Experiments were started with silicon cells (copper dummy cells were used in Phase I) laminated between two glass plates using polyvinyl butyral (PVB). Not unexpectedly, the initial results have shown cracked cells, but the laminations have been free of air bubbles. It will be necessary to work out the proper schedule of temperature and pressure to eliminate cell cracking.

A total of six 12- by 16-in. samples, each with nine interconnected cells, has been laminated, using an existing production process. This consists of rolling and heating the glass/PVB/cell/PVB/glass sandwich to expel as much air as possible, as well as sealing the edges. The sandwich is then autoclaved at 275°F and 150 psi, which completes the flow of the PVB around the cells, and drives all remaining air into solution with the PVB.

Because an extended cell array has triangular voids between cells, the PVB must extrude from the cell face into the void at some time during the process. Ideally, most of the flow should take place during the initial rolling/heating sequence, so that a minimum of air remains for the autoclaving. Sufficient flow must be obtained to seal the edges of the sandwich; otherwise, no pressure differential can be produced on the autoclave.

With the vendor's production line set for a standard process, it appeared that the temperature is too low to allow flow of PVB at low roll pressures. At higher roll pressures, the cells and/or glass will crack. Better flow will occur for thick PVB (0.030 in. each side), but such a product will be uneconomical with PVB cost becoming 80¢/ft², or approximately 14¢/W for materials. Our target is 0.030 in. of PVB total, but it has not been possible to laminate by the roll process. At this time it is not likely that the line will be made available for experiments with temperature, time, and pressure. In the vendor's opinion, a higher temperature is self-defeating because premature edge sealing will occur, trapping excess air.

We have also assessed the results of inserting triangular pieces of PVB between cells, to minimize the void volume. Laminations are successful (no air bubbles) with this method, using 0.015-in.-thick PVB both sides, although some cells are broken. Round inserts work equally well.

Further tests will readdress the use of a vacuum bag. In this method, the entire heating/pressure cycle is done in the autoclave, and variations in process can be made.

4. Panel Lamination - Acrylic Casting

An alternative to PVB laminating is being explored as a backup process. Methyl methacrylate-butyl acrylate resin is one of the cheapest materials available and has excellent weathering properties. Although experience has shown that acrylic encapsulation alone tends to crack at low temperatures, a combination of methyl methacrylate and butyl acrylate between glass plates provides a relatively soft inner core that is expected to survive the required temperature extremes of -40 to +90°C.

Because the acrylic monomer can be cast between glass plates spaced 0.020 to 0.030 in., the estimated cost is 3 to 4¢/W for the material.

Initial work has shown some good news and some bad news. The liquid monomer has a low viscosity and wets glass and silicon surfaces quite readily. This allows filling of the volume between glass plates - including the cells - with exclusion of all air. When cured, the acrylic adheres to the glass as well as PVB does (an acrylic acid additive is included to promote bonding).

Procedural problems do exist, however. The monomer shrinks about 20% in volume during cure, and therefore requires that a reservoir be provided for makeup into the panel. Because that is a nuisance, we have postulated that over-filling the volume by 20% (allowing the glass to bulge slightly) will be successful. Experiment seems to verify this, although the transverse shrinkage is clearly not uniform in this case since the edges must be clamped. If the cure is too fast to allow adjustment of volume, local regions of low pressure due to shrinkage are produced, and the response of the uncured monomer is to form bubbles. These bubbles are permanent once formed. We speculate that it might be possible to put a nearly cured panel into an autoclave and complete the cure at high pressure to cause enough internal flow to prevent formation of bubbles.

If the acrylic casting can be made to work, the following sequence would be amenable to automated production (with some human interaction):

- Cells pretabbed
- Cells placed in soldering fixture
(external conductors placed manually)
- Cell array mass-soldered
- Cell array cemented to rear glass plate with hot-melt adhesive stand-offs (provides cell separation from glass sheet)

- Top glass plate sealed over cells with elastic sealant around edges
- Assembly filled with monomer and sealed off
- Cure
- Assemble frame and electrical hardware (manual)

SECTION IV

PLANS FOR NEXT QUARTER

A. JUNCTION FORMATION

1. POCl_3 Diffusion

We shall continue to process lots of wafers having ~ 30 ohm/square sheet resistance and junction depth of about $0.4 \mu\text{m}$ for screen printing.

2. Ion Implantation

Work on low temperature annealing will be started. Also we shall begin to prepare 3-in.-diameter cells by ion implantation.

B. SCREEN-PRINTED METALLIZATION

The screen printing process will continue to be evaluated for both front and back sides of solar cells. We shall begin to investigate the interactions between the inks and the silicon and try to establish the necessary and sufficient conditions for an ink to make a low resistance contact to the n-diffused silicon.

C. SPRAY-ON ANTIREFLECTION COATING

We plan to work on process control techniques and develop the optimized subprocess steps into one integrated production process. We shall verify this with the coating of active cells.

D. SOLDERING TECHNOLOGY

We will construct a soldering "over" for mass-soldering a 4- by 4-ft cell array to demonstrate feasibility of one-shot reflow. In addition, we plan to assess viability of screen-printed cells with reflow operations and assess the effects of temperature cycling soldered joints over 130°C range.

E. PVB LAMINATING

We will determine an appropriate time/temperature/pressure process schedule for vacuum bag/autoclave process that will allow 0.015-in. thickness of PVB (2 layers) without breaking cells or leaving air bubbles. We will subject laminated samples to temperature cycling, -40 to +90°C, and increase panel sample size to approximately 2- by 2-ft (40 cells plus bus bar).

F. ACRYLIC ENCAPSULATION

We plan to include active cells within a 12- by 18-in. panel, including external connections and we will increase the size to 2- by 2-ft if results warrant. A method of cell handling must be developed.

We will also investigate proportions of methyl/butyl monomer as they affect curing and environmental properties.