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DEVELOPMENT OF LOW COST CONTACTS TO SILICON SOLAR CELLS

Second Quarterly Report for July 15–October 15, 1979

By
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Work Performed Under Contract No. NAS-7-100-955244

Optical Coating Laboratory, Inc.
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City of Industry, California

MASTER

U.S. Department of Energy

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Solar Energy

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SECOND QUARTERLY REPORT

FOR PERIOD COVERING
15 JULY 1979 TO 15 OCTOBER 1979

BY

D.P. TANNER AND P.A. ILES

JPL CONTRACT NO. 955244

OPTICAL COATING LABORATORY, INC.
PHOTOELECTRONICS DIVISION
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"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

ABSTRACT

This report states the present results of the second phase of the contract in developing low cost contacts to silicon solar cells using copper. In Phase I, copper diffusion from the newly developed plated Pd-Cr-Cu contact system with heating of 400°C was shown to cause shunting problems in active solar cells. Phase II started with a literature search on reported details of copper diffusion through different metals. Nickel was shown to be the best easily plated candidate metal to serve as a barrier to the copper diffusion.

A heat treatment study using evaporated metals is in progress to evaluate the results of the paper study. Thus far Pd-Ag, Cr-Ag and Pd-Cu systems have been studied.

A inexpensive screenable plating mask has been found and when used with a newly developed contact pattern gave cells with good V_{OC} , I_{SC} and curve fill factor.

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INTRODUCTION*

The contract involves evaluation of the technical feasibility and effective cost of a copper plating system for the manufacture of solar cells for high volume production of low cost solar array (LSA) modules. The LSA goal is to provide low cost silicon solar cells formed into operational arrays. At present, the cost breakdown shows that about 1/3 of the array cost is in materials (silicon and metals), slightly more than 1/3 for processing into cells, and the remainder for array formation. Much of the LSA effort (Tasks 1, 2) is aimed at reduced silicon cost; other effort in Task 4 is aimed at process cost reduction and at automated processing. Other efforts are directed towards cell interconnection and encapsulation. Already the projected silicon costs show promise of reaching the near-term LSA goals, although as the minimum array efficiency goals are increased, more attention is being paid to the adequacy of lower cost silicon for use in high efficiency arrays. In most cases, it appears that the silicon cost goals may be achieved. Also many of the individual cell process steps appear to be capable of cost reduction to fit the goals.

The major process costs are those involved with the metallization required to contact and interconnect the cells. The costs of metals is rising, and with present understanding it appears that at least 1.6×10^{-4} cm³ of good conductivity metal will be needed for each cm² of cell area; this is an irreducible cost factor. It is, however, important to provide this minimum amount of metal with as little waste (or even reclaimable) metal as possible. It is for this reason that

*Taken from First Quarterly Report, repeated for convenience.

Careful analysis is proceeding on vacuum evaporation systems (where over 90% waste metal is used in depositing fine metal pattern), or of silk screened systems, where equivalent excesses are involved, although with greater ease of re-use.

Of all present methods, plating is most attractive in reduced metal usage; with resist patterns applied to the cell surface to leave the required areas available for metallization, it is possible by plating to deposit metal only where required. Thus metal usage can be kept to the minimum, and in addition the fact that a high vacuum is not required makes plated contacts most promising for reduced costs.

There are other aspects of contacts which must be considered. To date, most of the field failures have been attributed to the cell contacts, either because of reduced cell efficiency showing thermal cycling, or after corrosion caused by exposure to the atmosphere. The latter problem can be reduced by improved encapsulation methods.

For metals such as copper there are additional concerns regarding possible cell degradation should the copper migrate into the cell. The degradation could be reduced diffusion length (reduced I_{SC}) or possible shunt mechanism, decreasing both CFF and V_{OC} .

With the above background, it is clear why plated systems merit study in the present program, and also why the required precautionary and proving-out tests have been included.

PAST WORK (PHASE I)

During Phase I of the contract (15 October 1979 to 31 May 1979) a plated contact sequence was developed which used copper as the main conductor. The sequence first used an immersion palladium bath* which deposited $\sim 50\text{\AA}$ of palladium. Next an electroless chromium bath deposited $\sim 2000\text{\AA}$ of chromium on the palladium sensitized areas of the cells. Last an electroless copper bath deposited $\sim 500\text{\AA}$ of copper on the chromium and was followed by an electrolytic copper step to deposit 3-4 microns of copper. Cells with good I-V curves as well as good contact adherence were made (see Figure 1). All cells made used a phosphorus diffused 7-14 ohm-cm p-type <100> oriented silicon with an aluminum alloyed BSF. The first cells were 2x2 cm in area but later the process was scaled up to 2 1/4" cells. These first cells had their contact patterns defined by photoresist techniques which were shown to be expensive for our process goals [1]. Forty (40) 2 1/4" diameter cells of this final process were delivered to JPL at the end of the first phase of the contract. Typical solar cell efficiencies of this group of cells are shown in Table 1 and Figure 2.

At the end of Phase I it was also shown that heat treatments of this contact system ($\sim 400^\circ\text{C}$ - 5 minutes) would cause severe shunting problems possibly due to copper diffusion into the cells [1]. This problem is the major reason for barrier studies in Phase II of the contract, to try and find means of stopping the copper diffusion.

*See Appendices A-E for the full procedures for all the processes used.

FIGURE 1

Plated Palladium-Chromium-Copper

FIGURE 2

TABLE 1
SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: 2 1/4" Solar Cells With Pd-Cr-Cu Plated Contacts

TEST CONDITION: AM1

TEMPERATURE: 28°C

DATE: 15 May 79

NO.	V _{OC}	I _{SC}	I _{SCB}	I _{SCR}	I _{Max}	V _{Max}	P _{Max}	CFF	η	AREA
	mV	mA	mA	mA	mA	mV	mW	%	%	cm ²
1	586	840	---	---	750	470	352.5	72	13.7	25.7
2	585	850	---	---	755	470	354.9	71	13.8	25.7
3	579	840	---	---	755	470	354.9	73	13.8	25.7
4	454	817	---	---	550	260	143	39	5.6	25.7
5	586	868	---	---	760	460	349.6	69	13.6	25.7

Cells had only approximately 30% current increase due to the CVD SiO₂ (only a plating mask).
These are five cells taken in random from the forty (40) cells delivered to JPL.

NEW WORK (PHASE II)

Paper Study

A literature search has been conducted to locate papers dealing with copper diffusion and/or interactions with different metallic barriers. It was preferred that the search be restricted to papers dealing strictly with diffusion studies using thin films, but during the search it was found that only a limited amount of data on thin films are available. Most sources use bulk samples in polycrystalline or crystalline form. The papers used a variety of techniques of measuring copper diffusion ranging from radioactive tracer experiments to use of an electron microprobe. Each diffusion measurement technique will be identified in the test, but will not be considered in the final data summary due to the limited data base of this study.

Data have been found on the following different metal systems: Cu→Ag, Cu→Au, Cu→Be, Cu→Cr, Cr→Cu, Cu→Fe, Cu→Li, Cu→Ni, Cu→Pd, Pd→Cu, Cu→Pt, Cu→Sb, Su→Ti, Cu→U and Cu→Zr. Also two papers were found on the Cr-Cu contact system, mainly dealing with contact stability.

As stated in the introduction, an evaporated contact study will be conducted to test the conclusions from the paper study. It is realized that plated metal layers are usually less dense than evaporated layers and that the results from the evaporation study may not apply to the plated layers. Hopefully the planned tests can still guide future research of plating metals.

Figure 3 shows a summary of the diffusion data found from the different sources [2]. The lines on the far left of the plot are the metals that act as the best copper barriers. The best metal appears to be platinum with nickel a close second. Nickel is then the best candidate for a cheap platable copper barrier.

HEAT TREATMENT STUDY

A heat treatment study using evaporated metals designed to test the results of the paper study experimentally has been started. The study monitors the V_{OC} , CFF and I_{SC} of active solar cells for degradation effects caused by the heating. Early experiments [1] have shown that when copper diffuses into an active solar cell, there is an immediate decrease in the cell V_{OC} without any change in the I_{SC} (with the expected decrease also of the curve fill factor). The purpose of this study will be to check experimentally if nickel is a good barrier to copper. The test matrix details are as follows:

- (i) All heat treatments will be made in nitrogen only.
- (ii) Properties of the solar cells will be evaluated before and after the heat treatments.
- (iii) Heat Treatment Details:

TIMES (Minutes)	TEMPERATURES (°C)				
5	400	450	500	550	600
15	400	450	500	550	600

- (iv) Cell tests will include two control cells with Ti-Pd-Ag contacts.

Thus far three contact systems have been investigated, as follows.

Palladium-Silver

Figure 4 and 5 shows the results of this contact study using 2000Å of palladium and 3 µm of silver. The effects of the Pd system without using copper were needed before the copper effects could be properly separated. The data shows the V_{OC} starting to decrease at temperatures at or above 550°C for the 5 minute heat treatment and at or above 550°C for the

FIGURE 4

2000Å Pd - Thick Ag

○: 5m Control
 •: 15m Control
 +: 5m Pd-Ag
 □: 15m Pd-Ag

FIGURE 5

⁰
2000Å Pd - Thick Ag

○: 5m Controls
●: 15m
+: 5m Pd-Ag
□: 15m

the 15 minute heat treatment. The cells I_{SC} indicated little change with the heating (notice these temperatures are close to those where the Ti-Pd-Ag control cells started to fail).

Chromium-Silver

Figure 6 and 7 shows the results of this contact study using 2000Å of chromium with 3 μm of silver. The chromium-silver system did not degrade the cells V_{OC} until temperatures above 500°C were reached both for the 5 minute and 15 minute heat treatments. Notice also this was where the controls started to fail. The I_{SC} showed again no significant decrease or increase.

Palladium-Copper

Thus far the only experiment completed used 1000Å of palladium and 3 microns of copper. Other experiments will be done using thicker palladium layers. From the paper study palladium is known to be a poor barrier to copper (see Figure 3). At 560°C for a 1000Å layer the cell could degrade in 51 seconds. The data in Figure 8 shows the degradation of the cells V_{OC} . Even the 400°C heat treatment shows a great decrease in the cells V_{OC} , showing palladium is a poor barrier. As the heat treatment temperatures increased, the voltage of the cells improved. This could be caused by a formation of palladium silicide which appears to be a better barrier to the copper diffusion than Pd alone. From Figure 9 the cells (especially at 400°C) showed ~10% decrease in the current. This could be caused also by the large amount of copper diffusing into the cells. Again the cells improved at higher temperatures, consistent with silicide formation.

FIGURE 6

2000Å Cr - Thick Ag

○: 5m Controls
 ●: 15m Controls
 +: 5m Cr-Ag
 □: 15m Cr-Ag

FIGURE 7

FIGURE 9

1000Å Pd - Thick Cu

○: 5m Controls
 •: 15m Controls
 +: 5m Pd-Cu
 □: 15m Pd-Cu

During the last months of the contract other contact systems both evaporated and plated will be investigated in the effort to identify a good barrier to the copper diffusion.

NEW PLATING MASK

A screenable plating mask material has been found that will withstand the plating baths of the present process (see Appendix E). The material is a solvent removable plastic made by Colonial Printing Ink Co. The mask material is printed on in the desired pattern and dried under a heat lamp for several minutes. Line widths $<.005$ inches have been obtained. Preliminary cost estimates indicate it is very inexpensive to use. See Appendix F for the print on mask procedures.

NEW CONTACT PATTERN

A new contact pattern has been designed for the 2 1/4" diameter cells. Figure 10 shows the basic pattern. In Phase I a photoresist pattern was used which required over 15 microns of plated copper to get a good curve fill factor. This was the primary reason of the low CFF in Figure 2. The new contact pattern by design will only require 5 microns of copper. The contact pattern will have a maximum of 12% contact coverage and a designed curve fill factor of 77%. Figure 11 shows I-V data for a typical cell made with the Phase I contact system and the new print on mask.

FIGURE 10

2 1/4" Diameter Contact Pattern

Contact Coverage: 12%

Grid Line Thickness: <5 mil

FIGURE 11

Plated Pd-Cr-Cu Solar Cell With Print-On Plating Mask

SCALE UP

Also during the second phase of the contract a scale up of the plating baths has been made. The baths are now capable of plating two cassettes of wafers at a time. Also the electrolytic copper bath has been scaled up to plate three 2 1/4" or 3" diameter cells front and back at the same time. All baths in the future will be scaled up to the 3" diameter wafer size.

CONCLUSIONS

The paper study has been completed resulting in the identification of nickel as the best candidate barrier metal. Some of the contact heat treat studies have been completed resulting in the predicted cell degradation where copper is involved.

An inexpensive print on masking material has been found to replace the photoresist step in the Phase I process. This mask with the newly designed contact pattern has produced solar cells with good I-V characteristics (before severe heating schedules).

WORK PLANNED

In the next period the full matrix of the contact heat treatment study will be completed. These results will be interfaced with the old plating process and a new plating process will be developed.

Also in an effort to simplify the process, since nickel is thought to be the best barrier, cells will be made using nickel only instead of chromium. These cells will be tested under the same condition as the original cells.

A contact pattern will be designed for 3" diameter cells. These larger cells will be made and evaluated.

NEW TECHNOLOGY

New processes have not been sufficiently developed to be reported as new technology. Any new developments will be described at completion of the contract.

REFERENCES

- [1] "Development of Low Cost Contacts to Silicon Solar Cells",
Semi-Annual Report, JPL Contract No. 955244 (Optical Coating
Laboratory, Inc., ASEC).
- [2] "Analysis of Copper Diffusion Through Different Metallic Barriers",
Paper Study, JPL Contract No. 955244 (Optical Coating Laboratory,
Inc., ASEC).

MILESTONE CHART

(Continued)

LEGEND: Scheduled Continuing Completed

MILESTONE CHART

TASK	1979							1980	
	JUL	AUG	SEP	OCT	NOV	DEC	JAN		
10. <u>Evaporative Test Matrix</u>									
A. Barrier Metals									
B. Barrier Metal Thicknesses									
C. Plating Mask Materials									
D. Time-Temperature Diffusion Rates									
E. Output Performance Characteristics									
11. <u>Low Cost Plating Mask</u>									
12. <u>Corrosion Protection</u>									
13. <u>Technical Reviews</u>									
A. Program Review	▲	▲	▲	▲	Δ		Δ		
B. Design Review	▲	▲	▲	▲	Δ		Δ		
C. Project Integration		▲			Δ				
D. Project Workshop									
14. <u>Documentation</u>									
A. Program Plan	▲								
B. Monthly Reports (Technical, Financial)		▲	▲		Δ	Δ			
C. Quarterly Technical Report				▲					
D. Draft Final Report						Δ			
E. Final Report								Δ	

LEGEND: Scheduled Continuing Completed

APPENDIX A

Electroless Copper

COMMERCIAL PLATING SYSTEM

- A) Dynaplate Activator 120
- B) Dynaplate Conditioner 101
- C) Dynaplate 240 Electroless Copper

All solutions made by Thiokol/Dynachem Corporation.

Use at room temperature.

This bath is used in the final contact sequence, but only Bath C. The thin layer of copper generated from this bath, makes the electrolytic copper adhere better. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX B

Electroless Chromium

ELECTROLESS CHROMIUM BATHS

Bath A

Chromium Fluoride	.15	gm/l
Chromium Chloride	1	gm/l
Sodium Citrate	7.5	gm/l
Sodium Hypophosphite	7.5	gm/l

The operating temperature was 85-95°C.

Bath B *

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>
Deionized Water	200 ml	1800 ml
Chromium Acetate	6 gm	42 gm
Nickel Acetate	.4 gm	28 gm
Sodium Citrate	8 gm	56 gm
Sodium Glycolate	8 gm	56 gm
Sodium Acetate	4 gm	28 gm
Sodium Hypophosphite	5 gm	35 gm

The operating temperature was 85-90°C.

*This bath formulation was selected for the final chromium plating sequence. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated May 31, 1979.

Formulations taken from "Electroless Plating Today" by Dr. Edward B. Saubestre.

APPENDIX C

Electrolytic Copper

ELECTROLYTIC COPPER SOLUTION

Deionized Water   1000 ml

H₂SO₄   30 ml

CuSO₄   200 ml

Solution used at room temperature. Cells plate ~.3 microns per minute at 7 mA/cm².

This solution was used in final contact sequence. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX D

Electroless Palladium

MOTOROLA'S PLATING SOLUTIONS

Immersion Palladium Bath*

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>
Deionized Water	300 ml	1800 ml
PdCL	.05 gm	.3 gm
HCL	1 ml	6 ml
NH ₄ F	20 ml	120 ml

Mixed in a sonic bath and used at room temperature in the dark.

Electroless Palladium Plating Bath⁺

Deionized Water	830 ml
HCL	4 ml
PdCL ₂	2 gm
NH ₄ CL	27 gm
NAH ₂ PO ₃ ·2H ₂ O	6 gm
NH ₄ OH	160 ml

*Bath was used in final process. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated May 31, 1979.

⁺Bath only used for certain experiments. Palladium costs were too high.

APPENDIX E

Contact Procedures

CHROMIUM-COPPER PLATED CONTACT PROCEDURE

1. Standard 2x2 cm substrates or 2 1/4" cells.
2. Photoresist and etch.
3. Immersion palladium bath (Appendix E).
  - a) Five (5) seconds 6% HF.
  - b) Immersion palladium bath for 5 minutes in the dark.
  - c) Scrub cell with Q-tip, deionized water rinse.
  - d) Remove photoresist with acetone.
  - e) Heat treat 15 minutes at 400°C in N₂.
4. Electroless chromium bath (Appendix C).
  - a) Five (5) seconds 6% HF.
  - b) Deionized water rinse 5 seconds.
  - c) Immerse cells for 15 minutes, rinse deionized water.
  - d) Heat treat 15 minutes at 400°C in H₂.
5. Dip in 6% HF 5 seconds and then 5 seconds dip in deionized water.
6. Immerse in Dynachem electroless copper solution for 5 minutes at 35°C.
7. Plate in electrolytic copper solution for 20 minutes at (7 mA/cm²) for plating front and back simultaneously. Procedure plates 4-6 microns of dense copper.

For more detailed procedure see Process Specification

Procedures, Contract No. 955244, dated May 31, 1979.

APPENDIX F

Screenable Mask Procedures

PRINT-ON PLATING MASK PROCEDURES

1. Add 5% by volume of the reducer ER-48073 to the ER-6055 plating resist and mix.
2. Silk Screen the resist on the top surface of the cells using a 1/8" distance between the screen and the cells.
3. Dry cells under heat lamps at a 2 ft. distance for 5 minutes.
4. The cells are ready for plating.

Mask Material: ER-6055 Blue H.B. Fine Line Plating Resist

Reducer: ER-48073

Company: Colonial Printing Ink Company
180 E. Union Avenue
E. Rutherford, NJ 07073

NOTE: The mask is removed on the same step as the photoresist was removed in Appendix I (Step 3d). Only the acetone is replaced by trichlorolthene.