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PHASE 2 OF THE ARRAY AUTOMATED ASSEMBLY TASK
FOR THE LOW COST SILICON SOLAR ARRAY PROJECT

Sixth Quarterly Report

By
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April 1980

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Solarex Corporation
Rockville, Maryland

U.S. Department of Energy

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SIXTH QUARTERLY REPORT

APRIL, 1980

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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."

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SUMMARY

Work in this second quarter of the program extension comprised portions of four experimental tasks. The task to study nickel plating on silicon oxide films has led to the finding that the plating solution dissolves oxide before depositing nickel. The electron microprobe study of nickel penetration of silicon has shown that sintering can be conducted for long times at 300°C but that problems may arise above this temperature, even though there is no significant penetration of nickel into silicon below about 450°C. Measurements on cells fabricated using plating times in the four to fourteen minute range indicate no degradation of cell properties as a result of contact with the plating solution in this time range, but do show evidence of poor contact quality if the nickel plate is either too thick or too thin. The task to assess the Motorola plating process is in its early stages, but it is evident that the process is a very complex and time consuming one.

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1. INTRODUCTION

This program is concerned with nickel/solder metallization of silicon solar cells. The program comprises several studies of details of the nickel plating process and culminates in an assessment of the Motorola plating process.

During this quarter work was performed on all four of the remaining experimental tasks.

1.1 Surface Oxide Thickness and Sintering Temperature

Surface oxides on silicon are recognized as a possible cause of poor reproducibility in the metallization process, and cells are usually sintered after the nickel plating step to improve contact adhesion and electrical properties, presumably through diffusion of the contact metal through the oxide and into the silicon.

This task is an experimental study of the influences of silicon surface oxide thickness and sintering temperature on the adhesion and electrical characteristics of electroless nickel plates on oxidized silicon.

1.2 Nickel Penetration of Silicon

Metallized solar cells are usually heated, under con-

ditions ranging from mild to severe, to improve the contact between the silicon and the metallization. A critical concern in the case of nickel metallization is the possibility of nickel diffusion at elevated temperatures through the front junction of the solar cell, an occurrence which would create paths of high current leakage and could effectively destroy the solar cell.

This task is a study of nickel penetration into silicon as a function of sintering temperature and time in a range that might be experienced in solar cell manufacture. Electron microprobe analysis is used to detect nickel diffusion into the silicon.

1.3 Effect of Nickel Plating Solution on Solar Cells

This task comprises measurements of electrical characteristics of cells fabricated using a range of nickel plating times in an effort to detect any detrimental effects to the p-n junction of the solar cell which might be caused by exposure to the plating solution.

1.4 Evaluation of Motorola Plating Process

The final experimental task is an evaluation of the Motorola plating process. (1) The Motorola process is a complex one involving several steps of palladium plating,

heat treatment and surface cleaning prior to the electroless nickel plating step. The Motorola process will be compared with the Solarex process, which is a simple electroless nickel plating.

2. SURFACE OXIDE THICKNESS AND SINTERING TEMPERATURE

A large number of diffused silicon wafers (phosphine diffusion on P type 100 Cz wafers) were oxidized using a variety of techniques, including heating in air, heating in steam and heating in oxygen. Oxide thicknesses were measured using ellipsometry.

Heating in an oxygen atmosphere proved to be the best method for obtaining uniformity and reproducibility of oxide thicknesses; uniformity of oxide thickness on any single wafer or within a single batch of wafers was extremely good, with variations greater than two or three Angstroms being unusual.

Initial efforts at plating nickel and sintering gave quite variable and confusing results, and eventually led us to believe that the electroless nickel plating solution was dissolving the silicon oxide films before depositing nickel, a very interesting and significant conclusion.

2.1 Dissolution of Silicon Oxide Films

We have conducted a series of experiments, again using ellipsometry to measure oxide film thicknesses, to determine conclusively whether or not the oxide film is being dissolved by the plating solution.

In the first of these experiments, a group of three silicon wafers with different oxide thicknesses were immersed in our electroless nickel plating solution at 90°C for 12 min, at the end of which time no nickel had plated on them. Oxide thicknesses were measured again and the wafers were immersed in the plating solution for 6 min more. Nickel plated on two of the wafers, and the oxide thickness was measured on the third one. This experiment is summarized in Table 1.

Table 1

Oxide Dissolution by Nickel Plating Solution

Operation	Results		
	Cell D	Cell E	Cell H
Measure oxide thickness	110 Å	157 Å	177 Å
Immerse 12 minutes	No Plate	No Plate	No Plate
Measure oxide thickness	55 Å	92 Å	114 Å
Immerse 6 minutes	Plated	Plated	No Plate
Measure oxide thickness	----	----	51 Å

In a second experiment, a standard electroless nickel plating bath (2,3) was used at 90°C without the nickel chloride. This bath contained 100 g ammonium chloride, 20 g sodium hypophosphite, 168 g sodium citrate, 250 ml conc ammonium hydroxide, and 1750 ml deionized water. Two cells were immersed in the bath for intervals of three

minutes and oxide film thicknesses were measured after each interval. Data are shown in Table 2.

Table 2

Oxide Dissolution Without NiCl_2

Time	Oxide Film Thickness	
	Cell E3	Cell H4
Before immersion	157 Å	177 Å
After 3 minutes immersion	108 Å	135 Å
After 6 minutes immersion	69 Å	82 Å
After 9 minutes immersion	Dark blotches (blue to golden brown) stained both cells.	

In a third experiment, a solution was used which was the same as that used in the second experiment except that the sodium citrate was initially eliminated and was added at a later point in the experiment. Results of this experiment are outlined in Table 3. The control wafer had no diffusion and no added oxide.

In this third experiment, extra NH_4OH was added before adding sodium citrate, because silicon dioxide is known to dissolve in strongly alkaline solutions, but the NH_4OH had no measurable effect.

Table 3

Oxide Dissolution Without NiCl_2
Initially No Sodium Citrate

Operation	Results (Oxide Thicknesses)		
	Cell H3	Cell E2	Control
Measure oxide thickness	177 Å	155 Å	---
Immerse 3 min, measure oxide	157 Å	131 Å	Blue-brown stain
Immerse 9 min, measure oxide	157 Å	133 Å	
Add 250 ml conc NH_4OH			
Immerse 3 min, measure oxide	157 Å	133 Å	
Add 168 g sodium citrate			
Immerse 3 min, measure oxide	152 Å	114 Å	
Immerse 6 min, measure oxide	71 Å	37 Å	
Immerse 3 min	Blue-brown stain on both cells		

Obviously the electroless nickel plating solution dissolves the oxide film from the silicon and nickel begins to plate only after the oxide thickness has been reduced to some fairly low level (about 50 Å or less). It is also clear that the plating solution minus the nickel salt dissolves the oxide, but that when both the nickel salt and the sodium citrate are left out the solution dissolves only a small amount of oxide before the dissolution stops completely.

The blue-brown stain is formed even in the absence of the nickel salt and the citrate. We do not know the identity of the stain, but the best guess would be that it is a lower

oxide of silicon or perhaps an oxyphosphorus silicon compound. We have observed this stain on cells from which nickel has peeled and also on cells where the nickel - silicon adhesion has appeared to be very good, and we do not know that it is harmful in any way.

Now that we know the plating solution dissolves the silicon oxide down to a thickness of about 50 Å or less before plating any nickel, this task is resolved to a comparison of silicon containing an oxide film of 50 Å or thicker with silicon from which the oxide has been stripped as completely as possible.

2.2 Nickel Plating

A number of diffused wafers were plated with nickel, some with oxide films and some without. All wafers were cleaned with HF (about 2.5%) to remove oxide, and about 70 Å of oxide was grown thermally in O₂ on approximately one-third of the specimens. A pattern of buses, each about 1.5 mm wide, was formed on the wafers using Kapton tape. The oxidized wafers were plated for 10 min at 90°C in the electroless nickel bath, while half of the unoxidized wafers were plated for 10 min and half for 6 min. The thickness of the nickel plate on the oxidized specimens was expected to be less than the thickness of a 10 min plate

but greater than the thickness of a 6 min plate on un-oxidized silicon.

2.3 Sintering

After plating, the Kapton tape was removed and specimens were sintered for 1 min on a hot plate at temperatures from 200°C to 300°C. Some specimens from each batch were not sintered. Temperatures above 300°C were not used because of our earlier observation of spontaneous nickel peeling from wafers sintered at 350°C or above. (4)

After sintering, the specimens were dipped in molten solder and tinned copper tabs, 1.75 mm wide, were soldered to the buses.

2.4 Tab Pull Tests

The complete fabrication process outlined in 2.2 and 2.3 was run on two batches of wafers, at two different times, and 90° tab pull tests were conducted on all of the tabs. The combined data are shown in Table 4.

The stains described in 2.1 were seen on a few wafers after pulling the tabs, but they appeared on both oxidized and unoxidized wafers.

Table 4

Tab Pull Data on Oxidized Silicon

Sinter Temp	Average Pull Strength (g)		
	70 Å Oxide 10 min plate	No Oxide 10 min plate	No Oxide 6 min plate
None	549	801	358
200°C	536	683	727
250°C	731	490	853
300°C	593	519	756

It appears clearly that the presence of oxide on the silicon surface prior to plating has no substantial effect on the contact adhesion.

It also appears that sintering has no useful effect, with the possible exception of the 6 min plate case, though even in this case the difference may not be significant because data scatter is always fairly large in this kind of experiment.

We are well aware that sintering, even as little as 30 sec at 200°C, can frequently bring about a great increase in adhesion in contacts which adhere only weakly without sintering, but the data of Table 4 demonstrate that excellent adhesion can be obtained without sintering (beyond a few seconds in molten solder).

2.5 Cells with Oxide Films

Oxide films were formed on a group of fifty (2½" round) cells by heating in air at 450°C prior to nickel plating. Measurements of oxide thicknesses by ellipsometry ranged from 35 to 80 Angstroms. The oxide was removed by treatment with buffered HF from twenty-five of these cells, and all fifty cells were then nickel plated and solder dipped. Light I-V curves were determined at AMI for several cells selected at random from each group, and tabs were soldered to and pulled from several cells in each group. Data are shown in Table 5.

Table 5

Oxide Effect on Cells				
Electrical Characteristics				Tab Pull Strength (g)
Set A				
Oxide removed	V_{OC} (mV)	I_{SC} (mA)	P_m (mW)	
High	580	774	280	1531
Low	542	652	233	28
Mean	551	740	253	765
S.D.	11	34	14	425
Set B				
Oxide - no HF				
High	585	784	290	1644
Low	546	738	273	113
Mean	558	763	280	794
S.D.	14	16	7	340

Electrical Measurements: Set A, 11 cells; Set B, 6 cells.

Tab Pull Data: Set A, 18 tabs; Set B, 24 tabs.

S.D. = Standard Deviation.

The cells which contained oxide appear slightly better in all characteristics, but the differences are not large relative to the standard deviations and there is no basis for suggesting that any real difference exists between the two groups.

This observation is exactly what would be predicted for the case where the plating solution dissolves silicon dioxide before depositing nickel.

3. NICKEL PENETRATION OF SILICON

In this task electron microprobe analysis is used in an effort to detect any diffusion of nickel into silicon as a result of sintering.

3.1 Silicon Preparation and Plating

Silicon wafers with phosphorus front diffusion were plated with nickel using the Solarex electroless nickel plating process (but with no pattern on the front surface).

3.2 Sintering

Several 1 cm squares were cut from the processed wafers and were sintered in an inert atmosphere (He or N₂) for varying times at temperatures from 200°C to 450°C.

Specimens sintered at 350°C and higher, cooled in the inert atmosphere, then exposed to air, peel when exposed to air. Nickel is adhering tightly when first exposed to air, and then peels gradually with time, beginning at the edges. Measurements of the surface resistivity of the silicon after peeling show very low values of resistivity, indicating that the remaining surface contains some nickel.

A phase change is reported to occur at 325°C in plated nickel films containing phosphorus. (4,5) The initial state

is reported to be a highly disordered solid solution of phosphorus in nickel, while heat treatment above 325°C produces two crystalline components, tetragonal Ni₃P and fcc Ni.

3.3 Specimen Preparation for Microprobe Analysis

A procedure was developed for mounting and angle lapping specimens for microprobe analysis. Specimens were mounted in Buehler Castolite (a polyester) and were lapped at an angle of 3.5° using successively finer grits down to 0.05 micron alumina for the final polishing.

3.4 Electron Microprobe Analysis

Several selected specimens were delivered to Tousimis Research Laboratory for electron microprobe analysis. Specimens selected had been sintered at the following temperatures and times:

200°C, 1 min (2 specimens)

300°C, 15 sec, 1 min, 2 min (2 specimens)

425°C, 12 min

450°C, 1 min, 2 min, 20 min, 30 min, 40 min.

Figure 1 shows a microprobe scan as well as a schematic diagram of the scan. It can be seen that the probe detects silicon through the nickel (the silicon trace does not go to

Figure 1. Electron Microprobe Analysis: Schematic of scan (above); data from a typical scan (below).

zero) and that the transition from silicon to nickel occurs over 10-15 microns of scan length (1 micron of depth is equivalent to 16.38 microns of scan length). This transition region is the region where nickel thickness is varying and the probe is detecting more silicon through the thinner nickel. Electron beam diameter was 1 micron.

The scan shows no evidence of nickel penetration of silicon, and it is typical of all of our scans until we reach the lengthier sintering times (20, 30, 40 min) at 450°C. In these latter scans we see the transition region expanding into the 100-200 micron range, indicating nickel penetration depths up to about 12 microns. Figure 2 presents an example of a microprobe scan of one of these specimens sintered for a long time at high temperature.

These observations are consistent with reverse bias dark leakage currents previously reported and outlined here in Figure 3, which showed little increase in leakage current after sintering for as long as 30 min at 350°C or 2 min at 450°C, but a very substantial increase after 3 min at 450°C.

It is also evident from the nature of the microprobe data that any penetration of the p-n junction by nickel will be detected earlier by electrical current leakage measurements than by electron microprobe scans.

Figure 2. Electron microprobe scan of specimen sintered for 40 min at 450°C.

Figure 3. Nickel Sintering and Leakage Current

4. EFFECT OF NICKEL PLATING SOLUTION ON SOLAR CELLS

A number of solar cells were fabricated in which nickel plating time was varied from four to fourteen minutes. Our standard electroless nickel plating solution was used at a temperature of 90°C. The cells are 2 cm squares cut from larger wafers and have a bus, about 1 mm wide, parallel to and close to one edge with six narrower conducting fingers perpendicular to the bus. These cells are essentially the same as the ones pictured and described earlier. (4)

4.1 Light I-V Characteristics

Measurements of light I-V characteristics have been made at AMO, and the data are shown in Table 6. Cells within each group were plated in three separate batches (e.g. the group of 11 cells with a 10 minute plating time comprises cells plated in three separate batches on three different occasions).

Little variation is seen in open circuit voltages, but the short circuit current and maximum power data show distinctly better cell quality resulting from the intermediate plating times (6-10 min), and this trend is especially obvious in series resistances.

Table 6

Influence of Nickel Plating Time on
Electrical Characteristics of Cells

		Plating Time (Min)					
		4	6	8	10	12	14
V_{oc}	white mV	559 (8)	561 (12)	566 (13)	569 (17)	565 (14)	574 (10)
V_{oc}	red mV	542 (9)	545 (12)	550 (13)	552 (15)	548 (14)	557 (10)
V_{oc}	blue mV	508 (11)	507 (16)	520 (13)	510 (20)	512 (22)	515 (20)
P_m	white mW	45.6 (3.1)	49.8 (3.0)	51.7 (2.7)	51.5 (3.0)	45.1 (6.8)	46.3 (3.3)
P_m	red mW	25.4 (1.9)	27.7 (1.1)	28.7 (2.4)	27.9 (1.7)	24.7 (5.1)	26.0 (2.8)
I_{sc}	white mA	114.7 (8.7)	121.6 (4.6)	121.9 (3.5)	121.8 (3.3)	110.1 (13.5)	113.7 (2.7)
I_{sc}	red mA	65.4 (3.1)	70.4 (3.3)	69.4 (3.4)	68.9 (1.7)	62.5 (8.9)	66.4 (1.7)
I_{sc}	blue mA	26.7 (2.7)	25.4 (2.3)	28.1 (1.7)	26.6 (3.2)	24.9 (2.4)	24.0 (0.8)
R_{series}	ohm	.279 (.145)	.209 (.077)	.179 (.047)	.168 (.053)	.249 (.137)	.266 (.084)
No. of Cells		8	9	13	11	18	11

Mean values and (standard deviations)

AM0 2 cm square cells

Cells plated for less than four minutes could not be solder coated successfully, and cells plated for 12 min or 14 min had obviously poorer contact adhesion than those plated for shorter times. In fact, front metallization lifted spontaneously from three cells plated for 14 min (electrical measurements were not made on these three cells).

These light I-V data do not suggest any cell deterioration resulting from exposure to the plating solution. The observations are best explained in terms of contact quality, with intermediate nickel thicknesses being obviously most desirable.

4.2 Dark I-V Characteristics

Measurements have also been made of forward and reverse dark I-V characteristics. Diode n-factors obtained from these data are shown in Table 7. This is an effective n-factor defined by the instantaneous slope at the maximum power point of a plot of $\log I$ (dark) versus V .

Table 7

Diode n-Factors

	Plating Time (Min)					
	4	6	8	10	12	14
n-Factor	1.86	1.93	1.75	1.83	1.80	1.98
(Std Dev)	(0.08)	(0.21)	(0.28)	(0.25)	(0.24)	(0.31)

Some variation is obvious in the data of Table 7, but there is clearly no trend with plating time. The n -factors have also been calculated from measurements of static V_{OC} and I_{SC} made at varying light levels, and, while the values are slightly different than those shown in the table, there is still no evidence of a trend with plating time.

Thus we conclude that the cell properties are not affected by exposure to the plating solution in a time range from 4 to 14 minutes, except for the effect of nickel thickness on contact quality.

This kind of experiment cannot, of course, tell anything about interactions which may occur between the cell and the solution before nickel deposition has begun.

5. EVALUATION OF MOTOROLA PLATING PROCESS

The Motorola metallization process (1) has been considered by Motorola "to contain the maximum number of process steps required for assured metallization of n-on-p solar cells with n^+ front surfaces and p^+ back surfaces." (6) Motorola has also cautioned, however, that "The process sequence reported here may require minor modifications to account for different types of solar cell substrates and to account for the previous processing history of substrates prior to metallization."

The Motorola process utilizes the standard electroless nickel plating procedure of Brenner and Riddell (2,3), but precedes the electroless nickel plating step with three steps of immersion palladium plating, one step of electroless palladium plating, two heat treatment steps and several cleaning and rinsing steps.

Our experimental work on this task is in its early stages, and we have not yet obtained any quantitative data. We have run through the Motorola process several times with mixed results. In some runs the plating occurs as advertised, but in other runs the plated metal peels spontaneously, usually during or immediately after the electroless palladium plating step. Wafers from which the metal has peeled

can then be successfully run through the complete process from the beginning. In all cases virtually 100% of the metal is lifted from the silicon in a tape peel test.

The most striking observation at this point in our experience with the Motorola process concerns its complexity. The Motorola process specification makes it clear that well over two hours is required to run through the whole process, even with no delays between steps, but the process contains a large number of steps so that even short delays between steps can add considerable time to the already lengthy process. The result is a very cumbersome process, even when conducted in a laboratory environment.

6. CONCLUSIONS

Silicon dioxide films on cells prior to metallization (using an alkaline hypophosphite electroless nickel plating solution) do not harm contact quality, beyond the effects of nickel thickness. The plating solution dissolves silicon dioxide before plating nickel. There can be problems related to surface conditions, but such problems are caused by other impurities, not by silicon dioxide.

Sintering temperatures should be limited to a maximum of about 300°C, and at this temperature lengthy sintering is safe but not essential. In many cases excellent contact adhesion is obtained from simple electroless nickel plating with no sintering beyond a few seconds in molten solder.

Variations in plating time from 4 to 14 minutes at 90°C do not affect cell quality, again excepting the effects related to nickel thickness. Nickel thickness affects the quality of the contact, and an intermediate nickel thickness is most desirable (estimated approximate range 0.5-1.0 μm).

7. WORK STATUS

The first four experimental tasks have been effectively completed, leaving only the task to assess the Motorola plating process. Some experiments similar to those used in the first four tasks will, however, be used in the study of the Motorola process, comparing results of the Motorola process with the results of simple electroless nickel plating.

Work is proceeding on schedule.

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