Dr. 2063

DOE/JPL/954847-80/7

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

Technical Quarterly Report No. 6, October 1—December 31, 1979

By
M. G. Coleman
R. A. Pryor
T. G. Sparks
D. L. Saltzman

Work Performed Under Contract No. NAS-7-100-954847

Motorola Inc.
Semiconductor Group
Phoenix, Arizona

DIST-355
NTIS 25

U.S. Department of Energy

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.

DISCLAIMER

"This book 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."

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 \$6.00
Microfiche \$3.50

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

TECHNICAL QUARTERLY REPORT NO. 6

1 OCTOBER 1979 - 31 DECEMBER 1979

MOTOROLA REPORT NO. 2345/7

JPL CONTRACT NO. 954847

PREPARED BY

MOTOROLA INC. SEMICONDUCTOR GROUP
5005 EAST MCDOWELL ROAD
PHOENIX, ARIZONA 85005

M.G. COLEMAN, R.A. PRYOR, T.G. SPARKS, D.L. SALTZMAN

THE JPL LOW-COST 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.

PROJECT NO. 2345

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
1.0	Summary	1
2.0	Introduction	2
3.0	Technical Discussion	4
3.1	Ion Implantation	4
3.1.1	Silicon Surface Layer Contamination	4
3.1.2	Unanalyzed Beam Ion Implantation	5
3.2	Plasma Etch Processes	9
3.2.1	Plasma Patterning	9
3.2.2	Plasma Texture Etching	18
3.3	Metallization	18
3.3.1	Nickel Plating	18
3.3.2	Copper Plating	22
3.3.3	Barrier Studies	24
4.0	Conclusions	31
5.0	Recommendations	32
6.0	Current Problems	32
7.0	Work Plan Status	32
8.0	List of Action Items	32
9.0	Milestones	32

LIST OF TABLES

<u>TABLE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
1	A Comparison of Conventional Ion Implantation and Ion Milling Equipment	7
2	Parameter Estimates of Unanalyzed Beam Ion Implanted Cells Prior to Metallization.	14
3	Electroless Nickel Formulation Using Nickel Sulfate	20
4	Low Stress Acid Copper Electroplating Solution Formulations.	23

LIST OF FIGURES

<u>FIGURE NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
1	Illuminated, one sun, voltage-current characteristic for non-mass-analyzed, ion implanted solar cell. Implant was performed at low energy with an ion milling apparatus.	10
2	Illuminated, one sun, voltage-current characteristic for non-mass-analyzed, ion implanted solar cell. Implant was performed at low energy with an ion milling apparatus.	11
3	Illuminated, one sun, voltage-current characteristic for non-mass-analyzed, ion implanted solar cell. Implant was performed at low energy with an ion milling apparatus.	12
4	Illuminated, one sun, voltage-current characteristic for non-mass-analyzed, ion implanted solar cell. Implant was performed at low energy with an ion milling apparatus.	13
5	Parallel plate plasma chamber	16
6	Logarithmic current versus voltage curves for solar cell plated with copper but with no nickel barrier layer. Severe degradation occurs after heat treatment.	26
7	One sun, illuminated characteristic curves for solar cell plated with copper but with no nickel barrier layer. Performance is thoroughly destroyed after heat treatment.	27
8	Logarithmic current versus voltage curves for solar cell plated with copper on top of a nickel barrier layer. No important changes occur after heat treatment.	28
9	One sun, illuminated characteristic curve for solar cell plated with copper on top of a nickel barrier layer. No perceptible change occurs after heat treatments.	29

All tasks have progressed according to plan during this reporting period. In this report, the ion implantation, metallization, and plasma etching processes are highlighted.

Replacement of the hydrocarbon vacuum pump oils in the ion implanter with perfluorinated polyether pump oils has decreased, but not eliminated the formation of a carbonaceous surface layer on implanted wafers.

Simulated unanalyzed beam ion implantation of boron for p-on-n cell fabrication has shown preliminary favorable results, showing better performance than control analyzed beam boron implants.

An ion milling machine was adapted for true unanalyzed beam implants. The results show that high quality solar cells can be made with a high current unanalyzed ion beam.

A new plasma etching unit has been obtained for patterning experiments. Preliminary experiments have been run. A polymerization effect of reactant gases has been observed, presenting a control problem. Changes in mask materials and gas compositions have been shown to eliminate this problem with the plasma patterning process.

A re-evaluation of electroless nickel plating bath compositions has led to a new bath which gives successful plating without the formation of an oxide layer on the silicon surface observed with the previous baths.

Low stress copper layers have been electroplated over electroless nickel. The layers show suitable properties for solar cells.

Cells have now been fabricated and heat treated with nickel-copper metallization. Nickel is shown to be a suitable barrier to copper diffusion into silicon.

2.0 INTRODUCTION

There is a high probability that flat plate solar photovoltaic modules will become a major source of electricity generation throughout most of the world, and that the silicon solar cell will be the preferred generating element. In order to provide a realistic framework on which to build an effective program of R&D and demonstration for silicon solar cell modules, a series of objectives has been established to lead to a 1986 goal of 70¢/peak watt. At this price, solar-generated electricity will be able to compete with electric power generated by any other means, provided the solar cell modules are sufficiently reliable (e.g., have a mean life of 20 years).

To reach the 1986 JPL goal will require several advancements: 1) a cheaper source of pure silicon, 2) a much more economical way of transforming the source silicon into large, thin, (essentially) single crystal substrates having a controlled geometry, 3) an economical, large module package that will protect the interconnected solar cells it contains for at least 20 years from degradation caused by exposure to the weather, 4) an automated process sequence that produces high efficiency, reliable, cheap solar cells, tests them, interconnects them, and encapsulates them, and 5) a large market, of the order of 500 Mw/year.

When the JPL/ERDA LSSA Project started, the Motorola Solar Energy R&D Department participated in the Phase I of the Automated Array Assembly Task. The Phase I study identified a few potentially powerful process sequences for silicon solar cell production, and experimentally verified the overall consistency of the process sequence. It concluded that no basic technological innovations were necessary for solar cell fabrication or encapsulation in order to meet the long range LSSA Project goals. Detailed economic analyses

were performed, based on today's technologies, and showed that it should be possible to meet the JPL cost projections for solar panels.

The overall conclusion of the Array Automated Assembly Task, Phase 1, was one of cautious optimism. The present program, for Phase 2, has as its objective the further development of specific process steps (in a particular, powerful process sequence) leading to a completely specified solar cell (and module) production process sequence. This sequence must be capable of a high degree of automation and control. A detailed economic analysis is a major part of the program to ensure that the most cost-effective approach is taken.

During the first part of the Phase II program, feasibility of the process sequence and its individual process steps were confirmed. This, the second part of the Phase II program, is concerned with specification of process control parameters and limits which will allow progress toward automation of the process sequence. The main objective of this contract is sufficient process control limit definition to permit advanced equipment prototypes to be designed for incorporation into an advanced pilot line facility.

3.0 TECHNICAL DISCUSSION

3.1 ION IMPLANTATION

Investigations have been performed to study potential control problems with ion implantation associated with the vacuum pump oil and to study the effects of an unanalyzed ion beam on solar cell performance.

3.1.1 SILICON SURFACE LAYER CONTAMINATION

A clean, film-free silicon is hydrophobic, i.e., water does not wet the silicon surface. Alternatively, such surface films as silicon dioxide (SiO_2), silicon nitride (Si_3N_4), and photoresist are hydrophilic, being completely wet by water. These properties are useful for control in wet chemistry processing steps, allowing definitive end-point detection when removing surface films from silicon.

A surface layer contamination has been observed on ion implanted surfaces and was previously reported in Monthly Technical Progress Report No. 9, April, 1979. The surface contamination was observed during wet chemical pattern etching of silicon nitride, and was evidenced by the fact that a clean hydrophobic silicon surface could not be achieved, regardless of the etch time. The contamination was tentatively identified as a carbonaceous layer formed on the silicon surface as a result of ionic bombardment of residual pump oil vapors in the vacuum system. Surface oxidation experiments to remove such a polymerized hydrocarbon layer were successful in restoring hydrophobic silicon surfaces, consistent with the presence of such a layer.

As recommended by Tsai et al (1), the hydrocarbon vacuum pump oils used in the ion implanter vacuum system were removed and replaced with

(1) M. Y. Tsai, et. al., "Study of Surface Contamination Produced During High Dose Ion Implantation, J. Electrochem. Soc.; Sol-St. Sci. and Tech., Vol. 126, No. 1, Jan. 1979, pp 98 - 102.

perfluorinated polyether pump oil. Examination of implanted surfaces then showed an improved ability to become hydrophobic, but not to the extent deemed desirable. Subsequent examination of the pump oils showed the presence of some residual hydrocarbons from the original pump oils. Apparently, sufficient quantities of these oils are still present in the system to cause difficulties. A thorough dismantling and cleaning of all vacuum components appears necessary to eliminate this residue. The results, while somewhat inconclusive, indicate the desirability of the perfluorinated polyether oils. Future vacuum systems for ion implanters should incorporate these oils from the start to eliminate subsequent contamination from the hydrocarbon oils.

3.1.2 UNANALYZED BEAM ION IMPLANTATION

Experiments examining the use of unanalyzed ion implantation have continued. First, the simulated unanalyzed beam experiments, described in earlier reports, have continued. Second, experiments have been initiated to implant with a totally unanalyzed beam.

While not all of the data is complete, ion implantation using all of the major beam peaks in a BF_3 ion spectrum has been shown to produce high quality photoresponse in silicon solar cells. Substrates of 7 mil thickness, nominally 0.1 Ω -cm arsenic doping, and smooth surfaces, have shown open circuit voltages in excess of 600 mV and very high fill factors. In all cases, the BF_2 component of the ion spectrum was implanted first, followed by other boron and fluorine components. The initial results show, in fact, the fluorine is performing some "gettering" effect. The use of a simulated unanalyzed beam certainly appears feasible based on these experiments. The potential problem of implanting trace impurities, however, remains unaddressed by these simulated techniques.

In order to address the possible implantation of trace impurities in an unanalyzed beam, implantation with a totally unanalyzed beam is necessary. In addition to eliminating mass analysis, a second change in Implanter design is desirable to accommodate a very high ion beam current. The change is to utilize a large area beam rather than a small area focused beam. If very high beam currents are focused to a small area, current densities would be very high. These high current densities are capable of causing significant localized substrate heating effects, thought now to be deleterious to device performance. Such localized heating effects, caused by the very high local dose rate, can be reduced or eliminated through the use of lower localized dose rates available through a large area, high current ion beam.

Both features of a totally non-analyzed ion beam and a large area beam are available through the modification of commercially available ion milling equipment. Modifications for safety, since phosphorus, arsenic, and some boron compounds are highly toxic, are necessary.

Ion milling equipment has many features desired for mass production of low cost solar cells. A comparison of similarities and differences between conventional ion implanters and ion millers is shown in Table 1. The ion miller has the desirable features identified for future implantation equipment.

The Solar Energy R&D Department at Motorola does not now possess an ion milling unit. Arrangements have been made, however, to modify a unit in another area for some preliminary experiments.

In an attempt to fabricate n-on-p junctions for solar cell devices with low energy, high beam current, unanalyzed ion implantation means, an experiment was organized to use a Commonwealth Scientific Ion Milling machine. This machine has a 4" diameter ion gun, 2.0 keV and 0.4 mA cm^{-2} capabilities. It was modified to accept the dopant gas, 15% PH_3 in 85% H_2 and to exhaust the waste gases in a safe manner.

TABLE 1

A COMPARISON OF CONVENTIONAL ION IMPLANTATION
AND ION MILLING EQUIPMENT

SIMILARITIES:

HIGH VACUUM

AREA DEPENDENT

UTILIZE ACCELERATED IONS

DIRECTIONAL

DIFFERENCES:

<u>CHARACTERISTIC</u>	<u>IMPLANTER</u>	<u>MILLER</u>
IONS	DOPANT SPECIES	MOSTLY ARGON
ANALYSIS	ANALYZED	UNANALYZED
ENERGY	5 - 200 keV	0.3 - 1.0 keV
CURRENT	1 - 10 mA	200 - 4000 mA
AREA	$<10 \text{ cm}^2$	$>200 \text{ cm}^2$
VACUUM	$10^{-6} - 10^{-5}$ TORR	$2 - 5 \times 10^{-4}$ TORR

Substrate material chosen for this first experiment was Wacker float zone 1.8 - 3.0 Ω -cm, chemically etched, nontextured. In order to establish useful ranges for the first attempt, various process parameters were given wide limits. The p+ back surface enhancement layer was fabricated by several means. Fifty percent of the wafers were ion implanted with B¹¹ at a concentration of $4 \times 10^{15} \text{ cm}^{-2}$, 25% were diffused with "standard" BCl₃, and 25% undoped. Both of these process steps were completed before the p-n junction was formed and both saw the anneal cycle that followed the ion "milling" process step. The last 25% was ion implanted and annealed with $4 \times 10^{15} \text{ atoms cm}^{-2}$ of B¹¹ just before metallization. No appreciable differences were seen between groups with different methods of back enhancement fabrication.

The n+ front surface was formed by utilizing the PH₃ + H₂ mixture in the ion miller. This was the first occasion that this species and mixture of gas had been used to achieve an ion beam in this machine; however, no difficulty was experienced at all.

The substrate stage has 8 ea. 3" diameter wafer capability and 4 ion milling runs were done at different accelerating voltages and exposure times. All the runs were done at about 0.10 to 0.15 mA cm⁻² of beam current. The first group was milled with 1.5 keV of energy and with each wafer passed in front of an aperture in a shield which allowed about 3 - 4 seconds of beam exposure on each wafer in turn. The second group was milled with 2.0 keV of energy with each wafer passing twice in front of the aperture for about 6 - 8 seconds of exposure. The third group was not shielded at all and all 8 wafers saw about 2 - 3 seconds of beam. The fourth group was not shielded and saw about 20 seconds of beam.

The anneal cycle was 15 min. at 850°C in N₂ followed by 120 min. at 550°C in N₂.

A mesa configuration on the cells was achieved by stacking all wafers in direct contact and plasma etching the edges of all wafers.

The AR coating was done by plasma oxidation for 10 min. and vacuum deposition of 700Å of Si_3N_4 and a further anneal of 120 min. at 550°C in N_2 .

The preohmic pattern was accomplished with standard photoresist methods.

The pre-metal probe of electrical parameters showed group #4 (20 sec. of beam) to be the only group worth metallization.

Metallization was done by immersion, electroless and electrolytic methods to form a Pd-Ni-Cu-Ni layering.

Testing before metallization gave the parameter estimates for the eight cells of group #4, shown in Table 2.

V-I characteristics following metal of 4 of the cells are shown in Figures 1 - 4.

The results of this experiment show that solar cells can be made with totally unanalyzed beam high current ion sources. The potential cost benefits of this technique demand that future efforts be expended in this area.

3.2 PLASMA ETCH PROCESSES

3.2.1 PLASMA PATTERNING

Ion-enhanced plasma etching of a metallization grid pattern in the silicon nitride layer has been demonstrated and a laboratory process defined. The technology goal is to selectively and simultaneously etch patterns for metallization on both sides of the silicon substrate without significantly etching the silicon beneath these ohmic areas. The feasibility of the process was demonstrated during the last quarter of this contract effort. Also, the process was shown to have the potential to accurately define the desired

FIGURE 1: ILLUMINATED, ONE SUN, VOLTAGE-CURRENT
CHARACTERISTIC FOR NON-MASS-ANALYZED, ION
IMPLANTED SOLAR CELL. IMPLANT WAS PERFORMED
AT LOW ENERGY WITH AN ION MILLING APPARATUS.

FIGURE 2: ILLUMINATED, ONE SUN, VOLTAGE-CURRENT
CHARACTERISTIC FOR NON-MASS-ANALYZED, ION
IMPLANTED SOLAR CELL. IMPLANT WAS PERFORMED
AT LOW ENERGY WITH AN ION MILLING APPARATUS.

11

FIGURE 3: ILLUMINATED, ONE SUN, VOLTAGE-CURRENT
CHARACTERISTIC FOR NON-MASS-ANALYZED, ION
IMPLANTED SOLAR CELL. IMPLANT WAS PERFORMED
AT LOW ENERGY WITH AN ION MILLING APPARATUS.

12

FIGURE 4: ILLUMINATED, ONE SUN, VOLTAGE-CURRENT CHARACTERISTIC FOR NON-MASS-ANALYZED, ION IMPLANTED SOLAR CELL. IMPLANT WAS PERFORMED AT LOW ENERGY WITH AN ION MILLING APPARATUS.

TABLE 2

PARAMETER ESTIMATES OF UNANAYLZED BEAM
ION IMPLANTED CELLS PRIOR TO METALLIZATION

<u>LOT NO.</u>	<u>WAFER NO.</u>	<u>OPEN CIRCUIT VOLTAGE</u>	<u>SHORT CIRCUIT CURRENT</u>
SC018	5	594 mV	1135 mA
	6	563	1110
	17	523	780
	18	593	1380
SC024	8	560	1080
	9	578	1200
	10	570	1230
	11	561	1080

pattern without intimate contact of the mask and cell. This should be significant in development of this process for production equipment operation. Further development of this process required equipment that more closely parallels a possible production configuration, so a new parallel plate Tegal plasma etching system was installed during October.

The new system is designed for process development and has many features not on the previous equipment. The new unit is a simple parallel plate, glass bell jar system which offers significant flexibility. As illustrated in Figure 5, there are two grounded electrodes with the RF powered electrode spaced between them. This is particularly suited to the simultaneous etching of both sides of the substrates. The reactive gases are uniformly introduced through holes in the grounded electrodes. The electrodes are larger and can accomodate (2) 4-inch diameter substrates or a 3 inch by 10 inch sheet substrate. Due to its larger chamber size and the glass bell jar, virtually all "wall effects" on the plasma are eliminated. The glass bell jar chamber also offers easy visual observation for process development, but could be replaced with an aluminum chamber in a production prototype. The power supply is the now common 300 watt, 13.56 MHZ RF oscillator. The unit has the additional capability of a variable pulsed power operation mode which may be very advantageous in optimizing the process and will be evaluated. There is also some adjustment capability for peak to peak RF voltage within the matching network induction coil. In addition, a higher vacuum pumping efficiency is realized with the new equipment, but may still need further improvement.

Tests were run this period after the equipment was installed. The results seemed more consistent with some improvement in uniformity. However, somewhat lower etch rates were experienced due to lower power density from increased electrode size.

FIGURE 5
PARALLEL PLATE PLASMA CHAMBER

After preliminary evaluation of the new plasma equipment, however, a major and persistent problem developed. There is a mechanism whereby polymerization of the fluorocarbon ions competes with the etching silicon nitride. The polymerization effect varies from a slight reduction in the nitride etch rate to causing a secondary etch mechanism under the etch mask in areas which should not be etched. Under certain conditions, polymerization of the reactant gases totally replaced all etching. Although it had been observed on occasion in the previous equipment, it is more prevalent at the lower pressures. The gas phase effects are also easier to observe with the glass bell chamber. The polymerization phenomenon is believed to be related to the low flow rate or long residence time of the gases in the RF field and to the selection of reactor materials. Increasing the pumping conductance of the vacuum system and increasing the oxygen concentration significantly reduced the polymerization. Also, the electrode spacing was increased to reduce the confinement of the plasma dark space sheath at the lower pressure required for ion enhanced etching. Plasma confinement increases the reaction of the plasma with the electrode surfaces and concentrates the field within the plasma resulting in increased polymerization. These steps basically eliminated the gas phase reaction but nickel and molybdenum components such as used for etch masks were found to also cause surface polymerization. It is thought that since nickel and molybdenum form volatile fluorides that these may act to initiate polymerization. However aluminum and copper form nonvolatile fluorides and do not promote fluorocarbon polymerization. A recent published study (2) verifies these assumptions and gives a qualitative theory of the polymerization mechanism that is found in low-pressure, long-residence-time plasma systems used for ion enhanced etching.

(1) J. W. Coburn and Eric Kay, "Some Chemical Aspect of Fluorocarbon Plasma Etching of Silicon and its Compounds", IBM Journal of Research and Development, Vol. 23, No. 1, January 1979.

3.2.2 PLASMA TEXTURE ETCHING

The development plasma etching equipment required to investigate the surface texturing by anisotropic etching of the <100> orientation silicon has been obtained. It is similar to the new Tegal plasma etching unit used for the ion-enhanced plasma patterning of the silicon nitride AR layer. The exposed metal surfaces are nickel plated to prevent etching by the chlorine base reactant gases. Chlorine base gases such as carbon tetrachloride (CCl_4) have been reported to attack and roughen exposed silicon when used for etching aluminum metal films.

Due to delays in obtaining appropriate equipment, few results have been obtained. However, an attempt was made to etch silicon in a large parallel plate reactor used for aluminum etching for IC devices. Some apparently textured areas were observed near the substrate edges. This however is inconclusive due to the extremely low etch rates obtained with the low power density of this reactor and the presence of other reactants. Nevertheless, some brief work has been reported by others on anisotropic etching of (100) oriented silicon using various chlorocarbon gases including CCl_4 (3). Anisotropic etch rate ratios of 35 to 1 were reported for (100) compared to (111) surfaces. The investigation to evaluate the process feasibility will begin after the new equipment is installed.

3.3 METALLIZATION

3.3.1 NICKEL PLATING

As reported previously, electrolytic nickel plating solutions and techniques have been used successfully to obtain adherent nickel layers plated directly to silicon solar cell surfaces. This success may be due in large part

(3) H. Kinoshita and K. Jinno, "Anisotropic Etching of Silicon by Gas Plasma, Japanese Journal of Applied Physics, pg. 381, Vol. 16, 1977.

to the ability to maintain an oxide free silicon surface immediately prior to nickel plating. With the electrolytic nickel solutions which have been investigated, no tendency to form oxide interface layers between the silicon and nickel has been observed. Interface oxide formation is believed to be the principal variable which detracts from the effective use of a Brenner-type (nickel chloride) electroless nickel plating solution.

A potential drawback of electrolytic nickel plating to bare silicon is the requirement of careful attention to the fixturing and jiggling arrangements which provide electrical contact to the cathodic solar cell. Because of the fixturing complexity (especially associated with the electroplating of bare silicon), it would be desirable to use an electroless nickel bath to form the silicon contact layer. Thus, a re-evaluation of electroless nickel solutions was undertaken.

Electroless nickel solutions routinely used by the semiconductor industry for plating silicon usually consist of nickel chloride and a sodium hypophosphite reducing agent in an ammoniacal bath maintained at proper pH by excess amounts of ammonium hydroxide. A complexer such as sodium citrate is also used. From past investigation of electroless nickel solutions, it appears that a basic, high pH solution is required to effectively plate silicon. Therefore, in re-evaluating the direct use of electroless nickel, chemistries were considered which were alkaline in nature but which used substantially different solution components. Baths using nickel sulfate rather than nickel chloride were prepared. The amount of ammonia required for pH control was reduced. Sodium pyrophosphate was used as a complexing agent. Both sodium hypophosphite and dimethylamine borane were considered for reducing agents. In general, no substantial difference was noted between the phosphorus reducing agent and the boron reducing agent with respect to plating silicon solar cells. Hence the less expensive sodium hypophosphite was chosen for further experimentation. The formula used for further experiments is given in Table 3.

TABLE 3

ELECTROLESS NICKEL FORMULATION USING NICKEL SULFATE

<u>REAGENT</u>	<u>CONCENTRATION</u>
Nickel Sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	25 g/l
Sodium Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)	50 g/l
Ammonium Hydroxide (58% NH_4OH)	22 ml/l
Sodium Hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	25 g/l

The performance of this electroless nickel chemistry has been studied by Schwartz (4) and Feldstein (5) for applications other than silicon plating. However, this solution has proven to give excellent performance when used at moderate temperatures (50°C - 70°C) to plate silicon. Direct plating can be initiated in a matter of seconds on clean, heavily or lightly doped n-type silicon, or on lightly doped p-type silicon. Some difficulty which has not yet been resolved occurs when trying to plate heavily doped p-type silicon, such as a BSF layer for an nt-p-p- solar cell.

To circumvent such difficulties, and to introduce a uniform, repetitive plating situation, a surface pre-treatment has been employed to prepare the p+ and nt silicon surfaces for simultaneous nickel plating. The pre-treatment consists of a short (2-4 min.) immersion in a dilute palladium chloride solution which deposits a very thin and adherent palladium film on all exposed silicon. This film need not be continuous but is dense enough to effectively catalyze the subsequent electroless nickel deposition. The immersion palladium solution has been described in previous reports and consists of palladium chloride in a dilute, aqueous ammonium fluoride solution.

After palladium sensitization and water rinsing, the solar cell is plated in the sulfate electroless nickel solution for about 4 minutes. This is sufficient to obtain a nickel contact layer on the order of $5000 \text{ \AA}$ thick. With this electroless nickel chemistry, no tendency to oxidize the silicon surface has ever been observed. The result is a nickel layer (with a very small percentage of palladium) which is in intimate contact with the silicon surface. This assertion is born out by the fact that very low temperatures (250°C) are sufficient to react the nickel-silicon interface to form nickel silicide (Ni_2Si), thus obtaining strong metal contact adherence.

(4) M. Schwartz, Proc. Am. Electroplat. Soc., 47, 176 (1969).

(5) N. Feldstein, RCA Review, 31, (2), 317 (1970).

Such rapid silicide formation at low temperatures is in agreement with studies found in the technical literature where vacuum deposited nickel layers are formed on freshly cleaned silicon surfaces. As much as 400 - 500 Å of nickel silicide can be expected after heat treatment at 250°C for 60 minutes (6).

3.3.2 COPPER PLATING

Additional experiments have been conducted with the formulations for electrolytic copper plating solutions. As reported in Technical Quarterly Report No. 5, a commercial acid copper solution, Lea-Ronal Copper Gleam PC, has been successfully used to plate solar cells. However, to minimize possible stress effects in the plated copper layer, low stress copper sulfate/sulfuric acid solutions based on formulations given by Lamb, et. al. (7), have been evaluated. Two formulas used are listed in Table 4.

Formula 1 provides a plating bath which has low internal tensile stress. Formula 2 provides an internal stress which can range from very low tensile to low compressive. These simple formulas have proven to give satisfactory plated copper layers over electroless nickel base layers. Copper layers as thick as ten micrometers can be plated in 5 to 10 minutes. Adhesion is excellent and stress appears to be no problem. Plating can be accomplished at room temperature.

Formula 2 has been adopted for routine use in evaluating the nickel copper solar cell metallization system. Results of cell tests will be reported later. One addition to the copper solution which may prove to be desirable is a brightening agent. Addition of a brightener can lower stress and improve ductility. A commercial brightener has been ordered and will be tested.

(6) K. N. Tu, W. K. Chu, and J. W. Mayer, Thin Solid Films, 25 403 (1975).

(7) V. A. Lamb, C. E. Johnson, and D. R. Valentine, Journal of Electrochem. Soc., 117, 291C (1970).

TABLE 4

LOW STRESS ACID COPPER ELECTROPLATING SOLUTION FORMULATIONS

FORMULA 1:

Distilled or Deionized Water, H_2O	to desired volume
Cupric Sulfate, $CuSO_4 \cdot 5H_2O$	87 g/l
Sulfuric Acid, H_2SO_4	14 ml/l

FORMULA 2

Distilled or Deionized Water, H_2O	to desired volume
Cupric Sulfate, $CuSO_4 \cdot 5H_2O$	187 g/l
Sulfuric Acid, H_2SO_4	21 ml/l

To test the ability of a plated nickel layer to serve as a diffusion barrier for an electroplated copper conductor layer, several heat stress experiments have been performed. Various samples have been heated in nitrogen to temperatures of 300°C and 400°C for times of 15 to 60 minutes. In all cases, no degradation of solar cell performance was noted when a plated nickel barrier was present, but catastrophic degradation, usually in the form of a total electrical shunt of the solar diode, occurred when no nickel was present.

As an example of stress tests, two cells were prepared with electroless nickel layers approximately 5000Å thick. These were nominally three inch diameter cells with complete metal coverage on the back and about 8% coverage for the metal grid on the cell front. The front grid pattern was formed by etching the ohmic pattern into an existing silicon nitride antireflection coating using photoresist techniques. Thus, the silicon nitride also serves as a plating mask for the selective plating of electroless nickel.

After nickel deposition the cells were heated at 250°C in nitrogen for 30 minutes in order to form an adherent contact by nickel silicide formation. When pull tested, similar cells prepared at the same time as the two test cells failed only through conchoidal fracture of the silicon under the pull test tab.

One of the two test cells was then etched in an aqua regia solution (3:1 HCl:HNO₃) to remove all of the nickel layer. This cell, and the cell with nickel still intact, were then both plated with copper in an acid electrolytic copper solution. The copper was plated to a thickness of about 8 microns.

At this point, current-voltage characteristic curves were measured for both cells. Measurements were made with no illumination and with simulated (tungsten quartz-halogen lamps) one sun illumination. In the dark, sufficient data were taken to plot the logarithmic current versus voltage curves. These curves conveniently display the behavior of low-level excess currents which directly influence solar cell fill factor. Under illumination, the standard solar cell characteristic curve was plotted to obtain values for open circuit voltage, short circuit current, efficiency, and fill factor. Before heat stress, both test devices are excellent solar cells, each with fill factors just exceeding 80%. Both cells were then heated to 300°C for 15 minutes.

Current-voltage characteristic curves for the two test cells for measurements taken both before and after heat stress are given in Figures 6 and 7 for the cell with the nickel barrier removed and in Figures 8 and 9 for the cell with the nickel barrier intact. The results are dramatic. The cell without the nickel layer is thoroughly destroyed. The cell with the nickel retains its excellent characteristics.

As indicated in Figure 9, the illuminated characteristic curve remains unchanged after heat stress for the cell protected with nickel. The only change occurs for very low level currents, as seen in the log I versus V curves of Figure 8. In contrast, the log I versus V curve for the cell with nickel removed, Figure 6, shows an enormous increase in excess current -- so much so that the cell characteristics are totally dominated by this current. The effect, as seen in Figure 7, is to lower the cell output voltage to less than one fourth of its original value.

The failure of the cell without the nickel barrier layer after just 15 minutes at 300°C is no surprise. It is expected that copper will easily diffuse on the order of 200 microns through silicon for this level of thermal stress. This

FIGURE 6: Logarithmic current versus voltage curves for solar cell plated with copper but with no nickel barrier layer. Severe degradation occurs after heat treatment.

FIGURE 7: One sun, illuminated characteristic curves for solar cell plated with copper but with no nickel barrier layer. Performance is thoroughly destroyed after heat treatment.

FIGURE 8: Logarithmic current versus voltage curves for solar cell plated with copper on top of a nickel barrier layer. No important changes occur after heat treatment.

FIGURE 9: One sun, illuminated characteristic curve for solar cell plated with copper on top of a nickel barrier layer. No perceptible change occurs after heat treatments.

is, in fact, about the same as the wafer thickness (7 mils) used for the test cells.

The test cell with the nickel barrier layer that suffered no ill effects after 15 minutes at 300°C was given an additional 45 minutes to effectively equal a total stress time of 60 minutes, four times longer than the first treatment. As observed in Figures 8 and 9, the additional time at temperature had no effect on the solar cell operating characteristic and had only minimal effect on the diode low level excess current. In fact, the cell fill factor was still maintained at 80%. Although improbable, the slight changes observed in the low current portions of the log I versus V plots of Figure 8 may be due to very small and localized pinholes in the nickel layer through which copper has penetrated. On the other hand, the slight increases may be due to nickel itself diffusing to the junction in localized areas, may be due to other impurities from the plating operation, or may be due to stress.

4.0 CONCLUSIONS

Several important conclusions can be drawn from the work performed during this period.

The most significant conclusion is that, based on cells fabricated with ion implantation from a modified ion milling machine, is that high quality solar cells can be made with high beam current unanalyzed beam ion implanters. This has major cost implications on ion implantation equipment.

A further significant conclusion is that cells can be made with a base-metal plated contact system of nickel and copper. Stress heat treatment of such cells has resulted in cells which still have 80% fill factors. Nickel proved to be a suitable barrier of copper diffusion into silicon. Other tests showed that some barrier to copper diffusion is required.

A major conclusion from the work performed during this period is that an adherent electroless nickel plating can be applied to silicon surfaces without the competing formation of an interfacial oxide layer. This is possible, however, only by major modifications to the composition of the electroless plating bath over baths previously employed.

A tentative conclusion is that substitution of perfluorinated polyether vacuum pump oil in an ion implantation system can avoid the formation of observed carbonaceous contamination surface layers on ion implanted silicon.

Polymerization of plasma gases can result in a process control problem. The problem can be eliminated through the proper choices of reactor materials, reactant gases, and reactor design.

5.0 RECOMMENDATIONS

No specific recommendations can be made at this time.

6.0 CURRENT PROBLEMS

No current problems have been identified.

7.0 WORK PLAN STATUS

Work is progressing according to plan, as modified.

8.0 LIST OF ACTION ITEMS

No items requiring unusual action have come to light during this report period.

9.0 MILESTONES

Status of program is shown in the Milestone Chart.

Milestone Chart

[illegible]

Milestone Chart (Cont)

	1	2	3	4	5	6	7	8	9	10	11	12	13
	A	M	J	J	A	S	O	N	D	J	F	M	A
DOCUMENTATION													
1. Revised Program Plan		▲											
2. Program Integration Meetings	▲				▲				▲				△
3. Program Review Meetings		▲		▲		▲		▲		▲		△	
4. JPL Workshops									▲				
5. SAMICS Cost Analysis				▲				▲					△
6. Monthly Technical Progress Report		▲	▲		▲	▲		▲	▲		△	△	
7. Quarterly Technical Progress Report				▲			▲			▲			
8. Final Report (Draft)												▲	
9. Final Report (Distribution)													▲
10. Financial Management Report		▲	▲	▲	▲	▲	▲	▲	▲	▲	△	△	△