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METALLIZATION OF LARGE SILICON WAFERS

Quarterly Technical Report No. 3, April 1—June 30, 1978

By
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MASTER

Semiconductor Group
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U.S. Department of Energy

Solar Energy

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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.

Project No. 2344

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ABSTRACT

Tests of numerous cleaning processes have been performed and evaluated for enhancement of the nickel-palladium metallization system (NPMS). An improved formulation for the NPMS immersion palladium bath has been developed and is discussed. NPMS heat treatment cycles have been refined and re-defined. Updated IPEG price analysis figures are presented.

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1.0 SUMMARY

Work on the Metallization of Large Silicon Wafers has continued on schedule. A review is presented of various experiments on silicon surface preparation. As was discussed in previous reports, silicon surface cleanliness is a primary factor in satisfactory initiation of the immersion palladium deposition. Numerous cleaning procedures have been tested. The results are given in this report.

An improved formulation for the immersion palladium solution has been developed, and the experiments leading to this improvement are described. A model is presented which coherently summarizes the results of various immersion palladium solution tests.

The heat treatment cycles required for the nickel-palladium metallization system (NPMS) process sequence are considered. Experiments concerning both the ambient gas used for heat treatments, and the temperature of the treatments, are discussed. Plating solution depletion rates and ambient light levels near plating baths are related to chemical plating bath control.

An updated version of the baseline nickel-palladium metallization system process sequence is presented. In addition, the materials cost of palladium chloride and lead-tin solder is updated and factored into the JPL IPEG price analysis.

2.0 INTRODUCTION

The Automated Array Assembly Task, LSSA Project, is concerned with a comprehensive assessment of the improvements in existing technology that may be needed to develop an industrial capability for low cost, mass production of very durable silicon solar photovoltaic modules and arrays.

This portion of the project involves investigation, advanced development, and characterization of a method, adaptable to large volume production, for the metallization of large silicon substrates which are suitable for use as terrestrial solar cells. The proposed metallization system is one which can be selectively plated to exposed silicon surfaces with no need to specially protect areas covered with a dielectric (such as an antireflection coating).

The metallization scheme is comprised of three layers. Palladium, through the formation of palladium silicide at elevated temperatures, forms the ohmic contact to the silicon surface. Nickel, plated on top of the palladium silicide/palladium layer, forms a solderable interface. Lead-tin solder on the nickel provides high conductivity at low cost, allows a convenient means for interconnection of cells, and yields some additional degree of protection against deleterious effects resulting from moisture ingress.

It is expected that this nickel-palladium metallization systems (NPMS) will exhibit superior reliability, and be sufficiently cost effective for inclusion in processing for future solar cell modules selling for less than 50¢/watt.

3.0 TECHNICAL DISCUSSION

3.1 PRE-PLATING SURFACE PREPARATION AND CLEANING EXPERIMENTS

As discussed in previous reports, pre-plating cleans of silicon wafer surfaces have been deemed to be of special importance for insuring repeatable and consistent selective plating depositions. In particular, in forming the initial NPMS (nickel-palladium metallization system) palladium layer with an immersion palladium plating, the silicon must be clean to guarantee an adherent and uniform palladium deposition.

Over the course of the NPMS process sequence development, several investigations have been performed to assess the effectiveness of various cleaning and surface preparation techniques. These experiments were conducted by first preparing solar cells by using the particular cleaning technique under consideration, and then attempting to deposit a palladium layer on the silicon surface using one of several formulations of immersion palladium solutions. The outcome of each experiment was evaluated by SEM (scanning electron microscope) examination of the plated surface. Some plated layers were abraded with cellulose swabs to test metal adhesion.

The first group of experiments utilized the fluoboric acid immersion palladium solution (HBF_4/ImPd) to study the benefits of various pretreatments which attack silicon, silicon dioxide, or miscellaneous organic contaminants. These pretreatments may be used alone or in sequential combinations. Five sequences studied are diagrammed in Tables 1 and 2.

If the silicon surface as-received for plating is already reasonably clean, then silicon dioxide etches using dilute hydrofluoric acid (HF) solutions, such

TABLE 1

PRECLEANS BASED ON THE ACID ETCHING OF OXIDES

CLEAN A

10:1 H₂O:HF etch

↓

DIH₂O rinse

↓

HBF₄ 1mPd

↓

SEM

CLEAN B

10:1 H₂O:HF etch

↓

50:1 H₂O:HF rinse

↓

HBF₄ 1mPd

↓

SEM

TABLE 2

PRECLEANS BASED ON SHALLOW ETCHING
OF THE SILICON SURFACE

CLEAN C

CLEAN D

CLEAN E

as outlined in cleans A and B of Table 1, are reasonably effective. However, more positive overall results were obtained with cleans C, D, and E which were capable of lightly etching the silicon surface in the solar cell ohmic contact areas. Clean C used a dry plasma etch (CF_4) technique while cleans D and E used wet nitric-hydrofluoric-acetic acid etch solutions. In addition, clean E incorporated a hot sulfuric acid clean, expected to attack organic contaminants.

Clean E, in particular, showed some promise of improved plating performance, and so a second group of experiments was performed to further investigate variations of this clean by using different silicon etch compositions and to establish whether a hot sulfuric acid clean would be sufficient without using the silicon etch. Cleans F and G in Table 3 use different ratios of nitric acid, hydrofluoric acid, and acetic acid in the silicon etch solution. If the silicon etch step is deleted, the clean H of Table 4 is obtained. Clean I of Table 4 is a simplification of clean H.

Cleans F, G, H, and I were evaluated with the immersion palladium solution which contains fluoboric acid (HBF_4 1mPd) and also with a solution in which the fluoboric acid was eliminated and the HCl content was increased. This particular solution (HCl 1mPd) closely resembles the well known solution of palladium chloride, hydrochloric acid, and water used to "sensitize" various metals and non-metals for subsequent electroless plating.

This second group of experiments (Tables 3 and 4) has indicated that sulfuric acid treatment is of some advantage in promoting improved plating. It also showed that a silicon etch greatly improves the immersion palladium layer plating uniformity.

Unfortunately, there are some major drawbacks to using a silicon etch. When working with shallow solar cell junctions, there is not much room for error while etching the silicon surface. The silicon etch rate must be precisely

TABLE 3

ADDITIONAL SILICON ETCH CLEANING PROCEDURES

CLEAN F

10:1:10 HNO_3 :HF:Acetic Etch (30 sec)

↓
 DIH_2O Rinse

↓
Hot H_2SO_4 Clean

↓
 DIH_2O Rinse

↓
10:1 H_2O :HF Etch

↓
50:1 H_2O :HF Rinse

↓
HCl 1mPd

↓
SEM

↓
 HBF_4 1mPd

↓
SEM

TABLE 3 (continued)

CLEAN G

TABLE 4

PRECLEANS DESIGNED TO REMOVE ORGANIC CONTAMINANTS

CLEAN H

CLEAN I

controlled or the junction is quickly penetrated and the device ruined; in fact, this effect was experienced. However, since plating occurred more evenly when the surface was lightly etched, that means there probably are contaminants present, during normal semiconductor processing, which tend to interfere with uniform plating initiation.

One type of impurity which might interfere with good plating behavior is a metallic impurity. Since test solar cell substrates are prepared for metallization by photolithographic patterning of the silicon nitride anti-reflection coating, and since photoresist is notorious for metallic contaminants, it is not unreasonable that metallic impurities may be left behind. For this reason, a cleaning approach which includes a metal etchant has been considered to be important.

In particular, an approach has been studied whereby solar cells to be plated are first given a plasma "ash" which oxidizes the silicon surface with an oxygen plasma. Any organic contaminants present during this step will be oxidized and volatilized. After chemically etching the silicon dioxide formed during the plasma clean, the cells are immersed in a metal etchant such as a hydrochloric acid solution or an aqua regia solution (HCl and HNO_3). Immediately before the immersion palladium bath step, the cells are rinsed in a dilute HF solution to guarantee an oxide-free surface. An example of this sequence is diagrammed in Table 5.

This type of pre-clean procedure has given consistent initiation of immersion palladium deposits with various solar cell test samples which have been fabricated. In the future, when photolithographic etching of metal contact patterns is eliminated in favor of more economical techniques, a less involved cleaning procedure may suffice.

TABLE 5

PRECLEAN SEQUENCE INCORPORATING BOTH
PLASMA REMOVAL OF ORGANICS AND
CHEMICAL ETCHING OF METAL IMPURITIES

3.2 DEVELOPMENT OF AN ADVANCED IMMERSION PALLADIUM CHEMISTRY

3.2.1 FLUOBORIC ACID BATH

The first step in the NPMS process uses an immersion palladium solution to apply the initial, thin palladium layer on the silicon solar cell surface. Until recently, the solution adopted in the baseline process sequence consisted of water, hydrochloric acid (HCl), palladium chloride (PdCl_2), and fluoboric acid (HBF_4). This solution has been discussed in previous reports.

However, several difficulties with the behavior of the fluoboric acid immersion palladium bath suggest removing it from consideration for further development even though some improvements have been achieved by using reduced PdCl_2 concentrations. For example, the growth of palladium nodules (see Figure 1) does not really agree with the assumption of a displacement reaction mechanism, even though this growth is to be expected with this bath since literature references allude to plating activation sites instead of depositing a continuous palladium film. Since a potential mechanical failure mode is separation at the silicon-palladium interface, this plating mechanism is especially subject to adhesion control problems. Examination of a silicon surface after a palladium layer has been separated gives the appearance of "pits" where the nodules were plated. The problem is not simply one of mechanical fracture, however, because these areas resemble etched (or chemically attacked) regions rather than mechanically fractured spots. This is illustrated in Figure 2. Another troublesome observation has been a heavy buildup of a dark residue, analyzed as silicon, around the end of the metal sintering furnace quartz tube. This is especially prevalent at the higher sintering temperatures of 600°C and 700°C .

(a) 5 minute immersion

(b) 5 minute immersion, rinse,
second immersion for 30 sec.

FIGURE 1: GROWTH OF IMMERSION PALLADIUM "NODULES" ON SILICON WAFER SURFACE
USING HBF_4 TYPE IMMERSION PALLADIUM SOLUTION.

(a) after mechanically scrubbing immersion palladium layer from surface.

(b) after peeling metal layers from surface. Photo shows a sectioned sample.

FIGURE 2: APPEARANCE OF PITTING ON SILICON SURFACE WHICH HAS BEEN PLATED IN HBF_4 TYPE IMMERSION PALLADIUM SOLUTION.

From the above observations, it may be concluded that the plating is initiated at existing surface sites or at only localized displacement sites. At these sites the nodules grow rapidly by a closed system electrolytic mechanism or by the formation of palladium salt complexes (palladium chlorides) which coplate with palladium. A coplating of palladium salts may explain the formation of the pitted surface after sintering and the poor as-plated strength. Etching of silicon by chlorine freed at 600°C during sintering may form a volatile silicon compound which would redeposit silicon when cooled. This would account for the silicon deposit on the quartz liner in our sintering furnace. These observations, combined with the continual problem of obtaining constant metal plating rates for the front (n-type) and back (p- type) surfaces, have forced a re-evaluation of the immersion bath chemistry.

3.2.2 AQUEOUS BATH WITH HYDROFLUORIC ACID

Assuming that a high HCl concentration may complex palladium chloride ions into more stable ions (which could also be deposited) HCl was eliminated from the immersion bath. Since palladium chloride is slightly soluble in water, a very dilute aqueous solution was made with approximately 0.01 g/liter of PdCl₂. Since we had experienced a stability problem with fluoboric acid and had doubts concerning the activity of the bath, hydrofluoric acid was substituted for the fluoboric.

The solution evaluated was

<u>CONSTITUENT</u>		<u>AMOUNT</u>
Water	H ₂ O	3 l
Palladium Chloride	PdCl ₂	0.02g
Hydrofluoric Acid	Hf	30 ml

The palladium chloride was dissolved at 70°C for 30 minutes, then allowed to cool to 30°C. Any undissolved residue was filtered, and the HF was added. Wafers were then plated for 10 to 15 minutes at 30°C.

The results were very encouraging; a thin palladium layer was plated, although palladium clusters were still present. (See Figure 3 for a scanning electron micrograph.) A great improvement in adherence was produced, with an undetectable amount of material being removed by vigorous swabbing. The PdCl_2 concentration was varied within the solubility limits with no apparent change in deposition rate. This should be expected with a true displacement reaction (1). However, slight variations in HF concentration did affect the plating rate. The generalized observations are illustrated in Figure 4.

Even though this bath did give the desired displacement layer, the bath was not acceptable. It had a slow deposition rate, and the low constituent concentrations made reproducibility difficult. An even more serious problem was the tendency to form anodic "oxide" films. This tendency could be reduced at higher temperatures (40°C), but at this temperature HF etching of the anti-reflection layer was accelerated.

3.2.3 AQUEOUS BATH WITH HYDROCHLORIC AND HYDROFLUORIC ACIDS

In an attempt to reduce bath sensitivity to variations in palladium chloride concentration, a small amount of hydrochloric acid was added. It was found that a molar concentration of HCl no greater than that of PdCl_2 was necessary to reduce the probability of forming complex ions. The bath has the same constituents of those listed in the literature (2) but at quite different concentrations. A typical bath used in these experiments consisted of:

(a) n+ front textured surface showing large Pd clusters on top of finegrained Pd layers.

(b) p+ back surface.

FIGURE 3: IMMERSION PLATED PALLADIUM LAYERS USING AQUEOUS, HF TYPE IMMERSION PALLADIUM SOLUTION.

FIGURE 4: GENERALIZED REPRESENTATION OF THE DISPLACEMENT PLATING MECHANISM; RATE VERSES PdCl₂ CONCENTRATION. THE EFFECT OF FLUORINE CONCENTRATION IS DENOTED AS A RATE CHANGE.

<u>CONSTITUENT</u>		<u>AMOUNT</u>
Water	H_2O	3 l
Palladium Chloride	$PdCl_2$	0.06g
Hydrochloric Acid	HCl (38%)	3ml
Hydrofluoric Acid	HF	10ml

With addition of the slight amount of HCl, the bath could be used at room temperature. Plating rate was increased, but the displacement layer had some loose nodules that could be swabbed off. The remaining layer was as good as the one produced from the bath with no HCl. The faster plating seemed to have reduced the formation of "oxide" films. By plating the wafers, swabbing off the loose material, and plating again, a thick continuous layer could be deposited. The bath, however, still etched the AR dielectric layer at an unacceptable rate.

3.2.4 AMMONIUM FLUORIDE IMMERSION BATH

When experimentation with hydrofluoric baths had reached the point of diminishing return, a concentrated bath consisting of $PdCl_2$ dissolved in a strong HCl solution similar to that preferred for metal (copper) substrates was tried. This was done to evaluate the role of HF in plating silicon. A reference for $SnCl_2/PdCl_2$ immersion plating of semiconductor material (3) suggested use of a fluorine acid predip to remove any oxides. This was evaluated to determine if a predip would be sufficient without producing etching of the antireflection layer. The immersion palladium bath consisted of the following:

<u>CONSTITUENT</u>		<u>AMOUNT</u>
Water	H ₂ O	800 ml
Palladium Chloride	PdCl ₂	0.25 g
Hydrochloric Acid	HCl (38%)	100 ml

A concentrated hydrofluoric acid predip was attempted with no success; plating did not initiate well, and the antireflection layer etched too quickly. However, an ammonium fluoride predip did initiate plating at a few spots, although the plated material was not very adherent. Addition of ammonium fluoride to the bath gave the desired immersion plating, but it also produced simultaneous plating of a thick nodular layer. This layer could be easily swabbed off leaving behind the adherent, thin immersion layer. By repeating this plating procedure, the immersion layer could be built up, but only after plating a considerable amount of extra material. This led to a series of experiments where the palladium and HCl concentrations were reduced by factors of two. The generalized relation which was determined for deposition rate versus Pd concentration is illustrated in Figure 5. The result of these experiments was a solution which gave an adherent, uniform immersion plated layer with reduced nodule formation (see Figure 6) with little or no visible residue removed by mechanical swabbing (see Figure 7). However, an effective layer for consistent initiation of electroless palladium was best obtained by using two plating steps and by swabbing before the second step. This ammonium fluoride bath did not etch the silicon nitride antireflection coating but the plating time was rather long for an efficient process. To minimize plating time, the ammonium fluoride concentration was increased; this resulted in a corresponding increase in plating rate. A slight temperature dependence has been noted but has not yet been evaluated. The current bath formulation is:

FIGURE 5: GENERALIZED REPRESENTATION OF NODULE PLATING MECHANISM RATE VERSES PdCl₂ CONCENTRATION. THE EFFECT OF HCl CONCENTRATION IS DENOTED AS A RATE CHANGE.

(a) N+ front textured surface showing large Pd grains on top of continuous, fine-grained Pd layer.

(b) P+ back smooth surface showing continuous, fine-grained Pd layer.

FIGURE 6: IMMERSION PALLADIUM PLATING FROM AMMONIUM FLUORIDE TYPE IMMERSION PALLADIUM SOLUTION.

(a) before mechanical scrubbing.

(b) after mechanical scrubbing

FIGURE 7: EFFECTS OF MECHANICAL SWABBING OR SCRUBBING ON IMMERSION PALLADIUM PLATING FORMED WITH AMMONIUM FLORIDE TYPE IMMERSION PALLADIUM SOLUTION.

<u>CONSTITUENT</u>		<u>AMOUNT</u>
Water	H_2O	3 l
Palladium Chloride	$PdCl_2$	0.08 g
Hydrochloric Acid	HCl	10 ml
Ammonium Fluoride	NH_4F	200 ml

This bath plates a thin metallic immersion layer with little or no loose nodules. The plated layer will withstand a vigorous mechanical swab with a Q-tip and will consistently initiate electroless plating.

3.2.5 IMMERSION PLATING MODEL

Observations from all of the experiments performed can be summarized by a generalized model of the mechanisms involved in immersion plating with the palladium chloride bath. This model is graphically represented in Figure 8. For the very dilute aqueous bath (Region A), a true displacement reaction occurs from the Pd^{+} ions in solution. The rate in this region is strongly affected by temperature and somewhat less by HF concentration. In Region C, the "loose nodule" mechanism is predominant. Although not entirely understood, this mechanism may be due to colloidal ionic complex radicals plating along with the metal. Several studies of the Sn-Pd solutions for activating of dielectrics have shown that large complexes, Pd_xCl_y and $Sn_xPd_yCl_z$ molecules, exist in a colloidal state (3, 4, 5). These colloidal complexes can also become ionic and participate in a cathodic plating mechanism. Reducing the HCl concentration should reduce this complexing, and, as expected, deposition rate was observed to decrease with lowered HCl concentration.

FIGURE 8: GENERALIZED DEPOSITION MODEL

Region A: Aqueous Solution Displacement Mechanism

Region B: Simultaneous Nodule and Displacement Mechanism (Current Process Solution)

Region C: Nodule Plating Mechanism with Little to No Displacement Plating.

The simultaneous formation of both a displacement layer and nodules over a wide range of concentrations occurs in Region B, Figure 8. Beyond some point, the displacement plating rate which is usually independent of concentration, begins to decrease with increasing PdCl_2 concentration. This is denoted by the lower dashed curve. In this region, nodule formation seems to proceed at a faster rate, and so the displacement reaction is reduced by some mechanism such as a surface masking effect or localized depletion of the reaction species. Some additional detailed research would be required to fully understand the process, but the proposed model can be used as a guide for the development of an optimized immersion palladium solution.

3.2.6 REFERENCES

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3.3 HEAT TREATMENT SEQUENCES FOR SILICIDE FORMATION

The baseline Nickel-Palladium Metallization System (NPMS) process sequence as reported in Quarterly Technical Report No. 1 required two heat treatment cycles for the reliable formation of an adherent palladium silicide (Pd_2Si) contact layer. These heat treatments have been routinely performed in a resistance heated furnace using tubular quartz sleeves, although it is expected that, in the long term, belt furnaces may be more appropriate. The original NPMS process sequence stipulated that heat treatment cycles be performed at 600°C in forming gas -- a mixture of 96% nitrogen and 4% hydrogen. Over the course of work on this contract, both the heat treatment temperature and ambient have been altered.

3.3.1 HEAT TREATMENT AMBIENT

Forming gas was originally chosen for the heat treatment ambient to prevent oxidation of the palladium layers during the silicide formation steps. However, the fact that hydrogen is known to quickly diffuse through palladium has presented some questions about potential palladium-hydrogen interactions. Any penetration and absorption of hydrogen into the palladium layer may effect palladium silicide formation at the palladium/silicon interface. If oxidation of the palladium surface were not a major problem, nitrogen alone may be a suitable annealing ambient. Hutchins and Shepela* have reported that a thin film of PdO was detected on Pd_2Si films grown in the temperature range of 550°C to 700°C . The thin PdO films that were formed could be etched in a dilute HF solution. However, Pd_2Si films grown at 350°C did not show the PdO surface film.

* G.A. Hutchins and A. Shepela, "The Growth and Transformation of Pd_2Si on (111), (110) and (100) Si," Thin Solid Films, 18 (1973) 343 - 363.

To determine the suitability of a nitrogen anneal, studies were performed to compare nitrogen (N_2) and forming gas ($N_2 + H_2$) ambients at three different annealing temperatures. The temperatures considered were $500^{\circ}C$, $600^{\circ}C$, and $700^{\circ}C$. Test solar cells were plated in an immersion palladium bath using the fluoboric acid (HF_4) type solution. (This plating deposits a thin, granular layer of palladium on the exposed silicon surfaces.) Scanning electron microscope photos were obtained for the plated palladium films before and after heat treatment. Six different anneals were tested, combining the three temperatures and two ambients.

In general, no problem was encountered in those tests where hydrogen was eliminated and only nitrogen was used. Where forming gas was used, there seemed to be a tendency for palladium grains to deform or to flow and "bead-up" rather than to be converted to adherent palladium silicide. Mechanically abrading the plated surfaces after heat treatment by using cellulose swabs indicated that, qualitatively, annealing in N_2 gave better adhesion than annealing in $N_2 + H_2$.

In other experiments, no difficulty was encountered during subsequent processing of samples annealed only in nitrogen. Pretreatments in dilute HF solutions (such as 10:1 $H_2O:HF$ and 50:1 $H_2O:HF$) were sufficient to prepare the palladium silicide surface of the samples for additional plating. Therefore, a forming gas ambient has been eliminated in favor of using a nitrogen ambient for the metallization heat treatment steps where palladium silicide is formed.

3.3.2 HEAT TREATMENT TEMPERATURE

Experience with the HF_4 immersion palladium bath had indicated that heat treatment temperatures between $500^{\circ}C$ and $700^{\circ}C$ were most satisfactory for obtaining adhesion of the immersion palladium and electroless palladium layers.

At lower temperatures, silicide formation did not seem to be adequately strong. These observations, however, are not supported by observations from the technical literature.

Hutchins and Shepela (previously referenced) have studied the rate of formation of Pd_2Si layers as a function of temperature and time. From their empirical data, they developed an analytical expression for the thickness (X) of the Pd_2Si formation for any given temperature (T) and time (t). The relation is

$$X^2 = K(T)t \quad (1)$$

where

$$K(T) = 7 \times 10^{-2} \exp \left(- \frac{29,200 \text{ cal/mol}}{RT} \right) \frac{\text{cm}^2}{\text{sec}} \quad (2)$$

R is the gas constant, $1.987 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1}$. Solving these equations for X, substituting the value of R, and converting the dimensions from centimeters to microns,

$$X(\mu) = \left\{ 7 \times 10^6 t(\text{sec}) \exp \left[- \frac{14,694}{T(^{\circ}\text{K})} \right] \right\}^{1/2} \quad (3)$$

Equation (3) gives the thickness of the Pd_2Si layer formed after annealing a film of palladium on a silicon surface. It is assumed that the palladium film is sufficiently thick to act as a Pd source for the duration of the annealing time.

Computations made by using equation (3) are presented in Figure 9. This figure can be used to estimate the various combinations of time and temperature which should be sufficient to form a Pd_2Si layer of a given thickness. For example, if a Pd_2Si layer which is 0.5μ thick is desired, an anneal of 10 minutes at 350°C should be sufficient. However, an equivalent anneal cycle would be 82 minutes at 300°C . Of course, such a 0.5μ layer of Pd_2Si can be obtained only if enough palladium (approximately 0.3μ or $3000\text{\AA}$) is present. In forming that layer, less than 0.2μ of the silicon surface will be consumed.

FIGURE 9: Pd_2Si layer thickness as a function of heat treatment time and temperature.

The curves of Figure 9 imply that there should be adequate palladium silicide formation rates at temperatures as low as 250 - 300°C. The discrepancy between the implication of these curves and the difficulty experienced in obtaining adhesion with low temperature anneal may be due to the nature of the plated palladium layer. If, as hypothesized in previous reports, the immersion palladium layer formed in a HBF_4 type bath contains a significant amount of palladium salt as well as palladium, this may account for slower silicide formation. The small percentage of phosphorus present in an electroless palladium layer may also impede rapid silicide formation, especially if the prior immersion layer has not been reacted sufficiently.

These discrepancies have been reconciled substantially by using the newly developed NH_4F immersion palladium solution rather than the HBF_4 solution. In fact, it has been confirmed that when using the NH_4F solution, annealing temperatures as low as 300°C are sufficient both for the anneal after immersion palladium and for the anneal after electroless palladium. Excellent adhesion is obtained. These results are apparently due to the improved nature of the palladium layer obtained with the new immersion solution. As plated, the thin film of palladium is very adherent and probably forms an intimate contact with the silicon surface in true displacement fashion. Furthermore, inclusion of palladium salts in the immersion Pd layer is minimized, if not eliminated.

Since the palladium layers in the nickel-palladium metallization system are limited to thin films intentionally, satisfactory heat treatments could be performed at almost any temperature between 300°C and 700°C. This is because the source of Pd on the silicon surface is limited, and therefore the thickness of the Pd_2Si layer (and its penetration into the silicon surface) will be limited. However, there are numerous benefits to be obtained by using the lowest practical annealing temperature. A lower temperature means that there

will be less oxidation of the palladium surface should some oxygen be present in the furnace atmosphere during the anneal; thus, subsequent plated layers may be applied with more control. At lower anneal temperatures, there will be substantially less possibility of palladium punch-through to the junction at silicon surface defects or areas of excessively thick palladium deposits. Furthermore, a lower temperature annealing furnace will consume less power and provide lower cost operation.

3.4 CHEMICAL PLATING BATH CONTROL

3.4.1 IMMERSION PALLADIUM SOLUTION DEPLETION RATES

The immersion palladium solution should be amenable to simple control and replenishment procedures. It is operated at room temperature, and its constituents are not readily evaporated. Solution pH is easily maintained. The depletion of palladium content is very predictable, and depends only on the area of exposed silicon placed in the immersion bath and the time for which it is immersed.

Some quantitative studies have been performed to determine the depletion rate of the NH_4F type immersion palladium solution. Figure 10 shows the measured change in palladium metal concentration in the immersion solution (in parts per million, PPM) versus the number of wafer-minutes plated, that is, the number of wafers plated times the time for which each was plated. (This method of representation is valid only for short immersion plating times because the preplacement process is self-limiting.) Data points are shown with a least-squares line drawn through them. The logarithmic relation is very explicit. The data of Figure 10 indicate that for the particular volume of solution tested (approximately 3 l), the palladium concentration was halved after 680 wafer-minutes.

FIGURE 10: IMMERSION PALLADIUM SOLUTION
DEPLETION VERSUS USE

It is expected that a series of similar studies for this process sequence would lead to a quantitative replenishment procedure for maintaining the immersion palladium solution at constant working strength.

3.4.2 AMBIENT LIGHT LEVEL

It was found, in the plating of solar cells, that ambient light level is important. The open circuit voltage generated by a cell, even while immersed in a plating solution, may be sufficient to initiate an electrolytic plating reaction, even in an electroless plating bath.

For example, an n-on-p solar cell may generate from 0.3 to 0.6 volt in ambient light conditions. This negative potential at the n-type front surface will cause the front to act as a cathode in the electroless solution and plate more rapidly than expected. (In some situations this may be desirable, but ordinarily it is not.) Electroless nickel and electroless palladium solutions tend inherently to plate n-type regions faster than p-type regions. A high ambient light level would accentuate this effect and cause an n-type solar cell front to plate much more heavily than a p-type back. This is undesirable since the front metal thickness must be carefully limited to be able to control metal penetration at the front junction and prevent junction punch-through; if the back plates much more slowly, its palladium thickness could be unacceptably thin. Consequently, electroless plating of solar cells is now done in the dark.

3.5 PRESENT BASELINE PROCESS

3.5.1 PROCESS SEQUENCE OUTLINE

A major advantage of the ammonium fluoride type immersion palladium solution described earlier in this report is that its incorporation into the NPMS process sequence has allowed the scrubbing step, which was included in previously reported sequences, to be eliminated. This surface scrubbing is no longer required to guarantee consistent and repeatable performance of the plated palladium layers. The present (revised) baseline process is outlined in Table 6.

3.5.2 IPEG PRICE ANALYSIS

A detailed exercise of the JPL Interim Price Estimation Guidelines (IPEG) analysis was presented in Technical Quarterly Report No. 2 for the nickel-palladium metallization system. Elimination of the scrubbing step, as discussed in the previous section, will impact the results of that analysis. Moreover, one of the prime cost drivers determined in the previous Quarterly Report was the cost of palladium chloride, the source of palladium in the immersion and electroless palladium solutions. It had been previously assumed that PdCl_2 was available at a cost of \$5.00/gram (in 1976 dollars). Recent investigation has led to a source of PdCl_2 available at a cost of \$1.66/gram (in 1978 dollars). This will significantly impact the previous IPEG analysis. Accordingly, this lower cost has been factored into the computations presented in Quarterly Report No. 2. On the other hand, the cost of tin has been rapidly increasing on the open market and this has caused the cost of lead-tin solder to rise rapidly. The original cost assumption of \$2.98/lb (1977 dollars) for 60 Sn/40 Pb solder has been replaced by \$4.33/lb. (1978 dollars). This higher cost for solder has also been utilized in revising the previous computations.

TABLE 6

BASELINE NPMS (NICKEL-PALLADIUM
METALLIZATION SYSTEM) PROCESS SEQUENCE

Starting Point: a) Solar cell with dielectric AR coat
 b) Pattern of desired metal contact etched into
 dielectric
 (Back surface may be totally bare or may be patterned.)

<u>STEP</u>	<u>PROCESS</u>
1	Immersion palladium coat (displacement reaction), room temperature solution.
2	Heat treatment (silicide formation), 300°C in nitrogen.
3	Electroless palladium plate (autocatalytic reaction), heated solution.
4	Heat treatment (additional silicide formation), 300°C in nitrogen.
5	Electroless nickel plated (autocatalytic reaction), heated solution.
6	Solder coat, lead-tin solder.

The summary of the revised IPEG analysis is presented in Tables 7, 8, and 9. In the original IPEG analysis, four separate cell geometries were considered: 7.6 cm diameter and 12 cm diameter circular substrates each with either full metal coverage of the cell back or with patterned back metal covering only 14% of the back surface area. Tables 7 and 8 give the add-on NPMS prices in 1975 cents/watt for each expense category of each process step as well as the totals for each category and each step. Table 7 is for the 7.6 cm solar cell and Table 8 is for the 12 cm solar cell. Table 9 summarizes the total add-on price for each of the four examples cited. For comparison, the results of the previous analysis are shown in parentheses. As can be seen, the present modifications have resulted in dramatic cost reductions for the NPMS system, enhancing its probability for meeting advanced cost goals.

TABLE 7
NPMS PRICES IN CENTS/WATTS (1975)
7.6 cm DIAMETER SUBSTRATES

PROCESS STEP	0.489 EQPT QUAN	96.9 SQFT QUAN	2.133 DLAB QUAN	1.255 MATS QUAN		1.255 UTIL QUAN	STEP TOTAL	
				21% METAL	107% METAL		21% METAL	107% METAL
1	.09	.16	.76	.15	.24	.12	1.28	1.37
2	.02	.02	.08	.01	.01	.00	.18	.13
3	.13	.20	.95	.51	2.07	.18	1.97	3.53
4	.02	.02	.08	.01	.01	.00	.13	.13
5	.10	.17	.82	.12	.28	.14	1.37	1.53
6	.08	.04	.19	.88	2.62	.11	1.30	3.04
TOTAL	.46	.61	2.88	1.67	5.23	.56	6.17	9.74

Prices are for 999,146 watts of 14% efficient (encapsulated) cells.

TABLE 8
NPMS PRICES IN CENTS/WATT (1975)
12 cm DIAMETER SUBSTRATES

PROCESS STEP	0.489 EQPT QUAN	96.9 SQFT QUAN	2.133 DLAB QUAN	1.255 MATS QUAN		1.255 UTIL QUAN	STEP TOTAL QUAN	
				21% METAL	107% METAL		21% METAL	107% METAL
1	.05	.09	.43	.11	.20	.07	.75	.84
2	.01	.01	.03	.00	.00	.00	.05	.05
3	.07	.11	.53	.47	2.04	.10	1.29	2.85
4	.01	.01	.03	.00	.00	.00	.05	.05
5	.06	.10	.47	.09	.26	.08	.79	.95
6	.07	.03	.16	.88	2.62	.09	1.23	2.98
TOTAL	.27	.35	1.65	1.56	5.12	.33	4.17	7.73

Prices are for 996,378 watts of 14% efficient (encapsulated) cells.

TABLE 9

REVISED NPMS ADD-ON PRICES (CENTS/WATT)

(For comparison, prices in parentheses are results of previous analysis reported in Technical Quarterly Report No. 2.)

SUBSTRATE DIAMETER	TOTAL CELL METAL COVERAGE (AS % OF FRONT SURFACE AREA)	
	107%	21%
7.6 cm	9.74 (18.03)	6.17 (10.39)
12 cm	7.73 (14.10)	4.17 (6.45)

JPL IPEG Analysis

Reference: 1975 Dollars

14% Encapsulated Cell Efficiency

4.0 CONCLUSIONS

Various pre-plating cleaning and surface treatment techniques have been evaluated, and several candidate processes appear to be acceptable. The most satisfactory clean studied to date has constituted a sequence of oxygen plasma ashing and aqua regia etching; this clean has minimized the effects of variable processing techniques prior to metallization.

Numerous formulations for an immersion palladium plating solution have been examined. In the course of these studies, a model has been developed to describe the effects of immersion (displacement) palladium plating reactions exhibited by these formulations. A much improved immersion palladium bath has resulted from this work. In fact, it is believed that a thin and very adherent displacement palladium layer can now be routinely formed on silicon solar cell surfaces.

Nitrogen (N_2) is an adequate ambient for heat treatment of palladium films to form palladium silicide (Pd_2Si). Forming gas is not required and is, in fact, likely to introduce additional problems if used.

The new ammonium fluoride immersion palladium solution permits effective use of low temperature annealing cycles. Results of heat treating layers formed with this solution seem to agree with behavior cited in the literature for vacuum deposited palladium films.

Electroless plating of solar cells in the dark permits simultaneous plating of front and back metal layers of acceptable thicknesses.

Elimination of the scrubbing step from the NPMS baseline process as well as more accurate reassessment of the supply costs of palladium chloride ($PdCl_2$) and lead-tin solder (60 Sn/40 Pb) have lead to an overall reduction of the add-on prices per watt compared to those prices presented in the previous detailed IPEG price analysis in Technical Quarterly Report No. 2. The price reductions

are significant. The new price tables in the present report indicate that the primary cost drivers are the materials costs for palladium plating and solder coating and the labor costs for the chemical plating steps.

5.0 RECOMMENDATIONS

It is recommended that the newly developed immersion palladium plating solution utilizing ammonium fluoride, hydrochloric acid, palladium chloride, and water be incorporated into the baseline NPMS process sequence. This would replace the original solution using fluoboric acid.

The heat treatment cycles used for the nickel-palladium metallization system (NPMS) process sequence for forming Pd_2Si should be done in a nitrogen ambient at a temperature of 300°C .

Electroless plating should be done in the dark if both front and back layers are plated simultaneously.

The cell scrubbing step previously included in the baseline NPMS process sequence has proven unnecessary with the revised immersion chemistry and should be eliminated.

6.0 NEW TECHNOLOGY

The following new technology item has been developed on this program:

Description: Improved, ammonium fluoride based, immersion palladium solution.

Innovator: Terry G. Sparks

Progress Reports: Technical Progress Report No. 5, April 1978.

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