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ANALYSIS AND EVALUATION IN THE PRODUCTION PROCESS AND
EQUIPMENT AREA OF THE LOW-COST SOLAR ARRAY PROJECT

Subject: Assessment of Metal Deposition Processes

Quarterly Report for April-July 1980

By
H. Goldman
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Contract 954976
Quarterly Report April to July 1980
(DRD Line Item 6)

Subject: Assessment Of Metal Deposition
Processes

January 1981

H. Goldman and M. Wolf

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.

Summary

After the influence of the metallization design on the performance of solar cells, particularly large area cells such as 10 cm x 10 cm size, has been analyzed, and a set of design rules derived from this analysis in the two preceding quarterly reports, this report deals with the available options for metal deposition. In its first part, the principles underlying the different options are described. These options include chemical deposition methods, both electroless and electrolytic, and physical methods, which comprise the various types of vacuum deposition as well as the thick film processes. The second part of this report contains a qualitative comparison of the practical aspects of the application of these processes to solar cell manufacturing. The next quarterly report will contain the detailed economic data of these options, and an evaluation of these data.

Table of Contents

	<u>PAGE</u>
Summary	ii
List of Tables	iv
I. Introduction	1
II. Brief Description of the Metallization Options	5
A. General	5
B. Chemical Deposition Processes	5
1. Immersion Plating	5
2. Electroless Plating	8
3. Electrolytic Plating	10
C. Physical Deposition Processes	13
1. Vacuum Deposition, incl. Sputtering	13
2. Thick Film Screen Printing	18
III. Comparative Evaluation of the Metal Deposition Options	21
A. General	21
B. Chemical Deposition Process	27
1. Electroless Plating	27
2. Electrolytic Plating	36
C. Thick Film Screen Printing	42
D. Vacuum Deposition	49
Conclusions	55
References	57

LIST OF TABLES

		<u>PAGE</u>
TABLE IA	Metallization Process Options	25 & 26
TABLE IB	Metallization Process Options	40
TABLE IC	Metallization Process Options c. Other Options	48

I. INTRODUCTION

The manufacturing methods for photovoltaic solar energy utilization systems consist, in complete generality, of a sequence of individual processes. This process sequence has been, for convenience, logically segmented into five major "work areas": Reduction and purification of the semiconductor material, sheet or film generation, device generation, module assembly and encapsulation, and system completion, including installation of the array and the other subsystems. For silicon solar arrays, each work area has been divided into 10 generalized "processes" in which certain required modifications of the work-in-process are performed. In general, more than one method is known by which such modifications can be carried out. The various methods for each individual process are identified as process "options". This system of processes and options forms a two-dimensional array, which is here called the "process matrix".

In the search to achieve improved process sequences for producing silicon solar cell modules, numerous options have been proposed and/or developed, and will still be proposed and developed in the future. It is a near necessity to be able to evaluate such proposals for the technical merits relative to other known approaches, for their economic benefits, and for other techno-economic attributes such as energy consumption, generation and disposal of waste by-products, etc. Such evaluations have to be as objective as possible in light

of the available information, or the lack thereof, and have to be periodically updated as development progresses and new information becomes available. Since each individual process option has to fit into a process sequence, technical interfaces between consecutive processes must be compatible. This places emphasis on the specifications for the work-in-process entering into and emanating from a particular process option.

The objective of this project is to accumulate the necessary information as input for such evaluations, to develop appropriate methodologies for the performance of such techno-economic analyses, and to perform such evaluations at various levels.

The reduction of quartzite to metallurgical grade silicon was examined, and the comparative evaluations of competing Czochralski techniques for growing single crystal, cylindrical ingots, and of slicing processes to produce single crystal silicon wafers were performed. The next "work area" for producing solar arrays is the fabrication of the silicon wafers to solar cells. This process involves many steps, one of which is the front junction formation. Of the major current junction forming processes, gaseous diffusion was examined in more detail. In addition, alternate options including modified diffusion processes and ion implantation were studied with respect to their potential as lower cost, mass production processes.

After junction formation, the next major step in cell fabrication is metallization. The metal pattern is needed

to collect and deliver the current from the photovoltaically active parts of the solar cell to a terminal where the load can be conveniently connected. We have examined the input work-in-process specifications, procedures, attributes, technical readiness, and costs for current and proposed major metallization processes, as well as the requirements for ancillary processes, such as masking, sintering, etc. These processes are: wet chemical plating which includes immersion, electroless, and electrolytic plating; vacuum deposition where the metal can be vaporized by thermal energy, by an electron beam, or by sputtering with Argon ions; and thick film screen printing of noble and base metals with and without the presence of frits. Also, variations of the above three processes were looked at. One example is the application of strike and sensitizing layers using plating. A variation of vacuum deposition is ion plating, where the vaporized metal atoms are ionized either by an Argon plasma or by an RF field. A variation of thick film screen printing is the Midfilm process which incorporates some aspects of the photoresist process.

Not only does the conduction layer have to be applied to the cell, but also its pattern has to be defined. The metal pattern is designed to minimize series resistance losses and area coverage. This report is concentrated on the options for applying the metal to the silicon surface. The process for pattern definition has not yet been examined equally extensively. In some cases, these processes are connected

with AR-coating formation, in others, they are an integral part of the metallization procedure, as in thick film screen printing.

As with our previous studies, the evaluations were started with the current methods of metallization for which a large amount of the needed information is available. Nevertheless, substantial gaps or uncertainties were found in important information required for both technical and economic evaluation of the currently practiced processes. In proceeding to the evaluation of processes which are still in the developmental or even conceptual stage, the gaps in needed information become very large. In these cases, it is necessary to fill the gaps more extensively with estimates based on extrapolations or analogies. Such estimates always leave some doubt on the accuracy of the evaluations, and it will be necessary to also make "probable error" estimates to reduce decision mistakes based on early evaluations. Nevertheless, collecting the information and carrying out evaluations at the earliest possible time provides not only a planning tool, but also aids in uncovering the deciding attributes about which information ought to be obtained at an early stage of the development process.

II. BRIEF DESCRIPTION OF THE METALLIZATION OPTIONS

A. General

Metal can be deposited in selected areas either by chemical or by physical processes. The chemical processes are usually called "plating". They are all so-called "wet" processes which means that deposition occurs from a solution. In the physical processes, metal is transferred in physically finely divided form, either as neutral or charged atoms or molecules, or as a powder, and re-constituted on the substrate as a contiguous metal layer.

B. Chemical Deposition Processes

The three major processes by which plating can occur from solution are immersion, electroless, and electrolytic plating. In immersion and electroless plating, all areas of the silicon wafer, which are not to be covered by metal, must be masked, that is covered by an adequately thick dielectric layer.

1. Immersion Plating

Immersion plating, which is normally used to plate "strike" layers of noble metals, such as Pd or Au, on bare silicon, is mainly due to a simple displacement reaction at the substrate surface. This reaction between the silicon atoms and metal cations results in an oxidation of the substrate and a reduction of the plating material. Probably the initial contribution of electrons to the metal cations

comes from the accessible dangling silicon bonds, followed by the breaking of silicon-silicon bonds which then leads to the formation of free silicon cations. The silicon ions then move into the bulk of the solution, and their charge is compensated for by the ambient anions. Because the plating cations entering the surface boundary region are reduced, which means converted to neutral atoms by the substrate, maintenance of charge neutrality at the substrate surface requires that equivalent substrate ions enter the solution. The chemistry of immersion plating can be elucidated by a Pd-plating solution whose constituents are approximately 1 wt% NH_4F , 1 wt% HCl , 0.0025 wt% PdCl_2 , and 98 wt% H_2O . The HCl increases the solubility of the PdCl_2 via the formation of weak complexes, while the NH_4F probably helps in keeping the oxidized substrate ions in solution. One possible displacement or immersion reaction at the substrate surface is:

or the reduction/oxidation might occur in stages, as in,

In any case, the final products are the plated palladium metal and the Si^{+4} ion. After the silicon cation leaves the surface boundary regime, its positive charge attracts chloride and fluoride ions, which by formation of complexes,

help to keep the silicon cation in solution. One possible complex formation is

There is only a small possibility for the formation of gaseous SiCl_4 since the silicon cation will hydrolysize (react with water) before it can form covalent bonds with a chloride anion.

For the immersion reaction to proceed, the material to be plated, or substrate, has to be more reactive than the plating metal. Too great a reactivity difference between the substrate and the plating cations in the solution would lead to a plating rate too high for the formation of dense and coherent deposits. The relative reactivity of the substrate and the plating cation can be adjusted by the addition of complexing agents such as a cyanide, ethylenedinitrolotetraacetic acid, (EDTA), or disodium salt. The complexing agent can, by binding with the oxidized substrate, drive the immersion reaction forward (reac (1) to the right) by effectively decreasing the concentration of those ions. Similarly, the driving force of the immersion reaction can be decreased by lowering the effective plating cation concentration by complexing.

One would anticipate that the immersion layer thickness would be limited to about $10 \text{ \AA}$, as the displacement reaction should cease, once the substrate is covered with a few atomic layers of plated metal. However, inhomogeneities or holes

in the thin plating layer permit the continuation of the displacement reaction. The holes result in local galvanic currents that keep driving the immersion reaction forward until the layer thickness is approximately 50-100 Å.

A disadvantage of the immersion plating solution is its limited capacity. The depletion of the metal cations, contamination from the plating surface, and side reactions contribute to the short life of immersion solutions.

2. Electroless Plating

In order to build up a thicker layer than can be achieved by immersion plating, electroless plating is often used. The material most commonly plated on solar cells using this technique is nickel. Also palladium, chromium, and copper can be plated electrolessly on silicon. In electroless plating, an oxidation-reduction reaction occurs catalytically at the substrate surface where the plating solution selectively reduces the plating cation. For example, in the nickel plating solution, the oxidation of phosphorus in a hypophosphite anion to an orthophosphite anion produces hydrogen atoms which are adsorbed on the substrate. It is the adsorbed hydrogen atoms (shown as H(ad) in reac (5)) that reduce the nickel cations to metallic nickel. The reaction mechanism in a basic, usually ammonium hydroxide, solution is thus:

For simplicity, the NH_4^+ and Na^+ cations, and the Cl^- anions are not shown in the above reactions. The notation S. indicates that the reaction only occurs at the substrate surface.

Since hydrogen is readily adsorbed on a palladium surface, a palladium layer is sometimes applied prior to the electroless nickel plating. Also, nickel can be plated directly on silicon, since there are hydrogen adsorption sites on silicon and silica. The density of potential adsorption sites on silicon, and consequently perhaps the coherence of the nickel film on this surface, is lower than on a Pd-surface. Another problem with plating nickel directly on silicon is that the thickness of the silica layer, which is always present on bare silicon, is thought to be a major factor in determining the adherence of the nickel. Also, too thick a native silica layer ($> 50 \text{ \AA}$) should result in excessive contact resistance and simultaneously poor adherence of the nickel. At the other extreme, a silica layer only a few atomic layers thick should permit a displacement reaction between the silicon and the nickel chloride to occur (immersion plating), so that the plating layer should not be expected to deposit smoothly.

The plating efficiency of the electroless nickel plating solution is lowered by several competing reactions that consume the hypophosphite anion without the production of adsorbed hydrogen. Two of these reactions are:

and

Because of the common ion effect, reaction (7) will occur to a greater extent in an acidic solution while reaction (8) will be more favored in a basic solution. To keep the electroless solution effective, precipitation must be minimized. Otherwise, the solution could plate out on itself, or on the container walls, starting with precipitated particles. In the nickel and chromium electroless plating solutions, sodium citrate, a chelating agent, is therefore used to keep the metal cations in solution. Another major constituent of the electroless plating solution is a buffer (weak acid or base and the salt of that acid or base). The buffer is used to maintain the pH of the solution in face of the hydronium ion consumption or production by the plating reactions.

3. Electrolytic Plating

Electrolytic plating, or electrolysis, is a very common commercial process, used either to deposit conducting, protective, or decorative surface layers, or to purify metals. Its first commercial application occurred over a century ago in the fabrication of silverware by silver plating. Electroplating can be used to deposit layers of substantial thickness and bulk metal properties, including conductivity. It differs from the two previously mentioned plating procedures in that energy for the plating is provided from an external

voltage source instead of a chemical reaction. The plating apparatus consists of an anode (the metal that is to be plated) and a cathode (substrate to be plated), both submerged in an electrolytic solution, usually parallel to one another and about 15 to 30 cm apart. Electrical connections have to be made to each workpiece (substrate), as well as the anode, from a dc power source capable of supplying the required current at a voltage between 4 and 9 volts (DC). Oxidation of the metal takes place at the anode, producing metal cations which are then transported, both under the influences of the applied potential gradient and of convection currents, to the cathode where the ions are reduced and thus plate out. In this process, the principal work of the external voltage is the movement of electrons from the anode to the cathode.

Since plating is a steady state situation (i.e., the number of electrons in the solution does not change in time), the mass of oxidized metal is equal to the mass of plated metal. The deposition rate can be derived from the current flow, using Faraday's Law which states that 96,500 coulombs will deposit one chemical equivalent. As one mole of electrons has a charge of 96,500 coulombs, a "chemical equivalent" has one mole of electronic charge. Thus, one chemical equivalent represents one mole deposition of singly charged cations, but only half a mole of doubly charged cations. Therefore, a current density of 1 mA/cm^2 would give a deposition rate of about 1×10^{-8} equivalents/sec-cm². This holds only if

the cathode and anode efficiencies are 100%. The electrode efficiency is defined as the actual mass deposited divided by the amount calculated by Faraday's Law.

In copper plating, the electrolytic solution consists chiefly of sulfuric acid and copper sulfate. The sulfuric acid is present in order to lower the resistivity of the plating solution, to prevent the precipitation of copper salts, and to increase the reactivity of the anode surface, while the copper sulfate is needed to charge-balance the oxidized copper in solution. Small quantities of molasses or other organics are sometimes added to the $\text{H}_2\text{SO}_4\text{-CuSO}_4$ solution to obtain finer grain deposits. The applied voltage for copper plating is 6 - 12 volts (DC), and the current density of the cathode is 40 - 60 mA/cm^2 . A higher voltage cannot be used to increase the current density, or the plating rate, since the reaction rate is limited by the diffusion of cations through the boundary layer (the Helmholtz double layer) from the bulk to the substrate surface. For electroplating copper directly onto an electroless deposited layer, or strike surface, of nickel, a $\text{H}_2\text{SO}_4\text{-CuSO}_4$ solution may not be suitable because of the possibility of an immersion reaction between the CuSO_4 and Ni. Immersion deposited copper is undesirable because it is not very adherent. Therefore, the nickel has to be initially coated with copper using an electroless solution, or with an electrolytic solution containing a copper complexing agent. The complexing agent effectively decreases the concentration

of copper in the solution, and hence, the driving force for a displacement reaction.

C. Physical Deposition Processes

The physical deposition processes are best separated into those transporting material divided into particles of molecular size, and those using much larger powder particles. The latter group is usually connected with the name "printing" processes, of which a substantial variety exists, but only one has gained significant application for metal layer formation in the electronic industry: screen printing. The first category includes those processes where the material is "vaporized" by heat, including that generated by an electron beam ("vacuum evaporation") or ion bombardment (sputtering), and then transferred as neutral particles by free flight through a gap narrow compared to a mean free path, to the substrate on which they are to be deposited. The other group in this category includes those processes where the particles are ionized and then accelerated by an electric field for their transfer to the substrate. These processes include plasma deposition and ion plating, a low-voltage variant of ion implantation.

1. Vacuum Deposition, including sputtering.

In vacuum deposition, the source (metal to be deposited) and the substrate (for instance silicon wafers covered with suitable masks) are both located in a vacuum chamber, where

the metal is evaporated and physically transferred onto the wafer. There are several methods for supplying sufficient thermal energy to vaporize the metal. A common laboratory method is to place chunks of wire pieces of the metal directly on a coiled filament, which is then heated by passing an electric current through it. This technique works well when the metal and filament wet each other, so that the filament will support the molten metal, when the vapor pressure of the metal is several orders of magnitude greater than that of the filament, and when there is no alloying between the metal and filament. The batch nature of this method and the small amount of metal that can be contained by the filament limit its practicality for large scale cell processing. In production processes, larger amounts of the metal to be deposited are contained in a crucible of graphite, refractory metal such as tungsten, or ceramic. The crucible is heated either by passing current through the crucible, or by a resistance furnace external to the crucible. A cap with a small orifice is usually placed on the crucible to avoid splattering and to gain directionality of the emitted metal vapor.

The coating thickness (t) obtained from a point vapor source of unrestricted opening angle to a planar surface follows Knudsen's cosine law, or:

$$t = \frac{m' \cos \theta}{4\pi r^2 \rho}, \quad (9)$$

where m' is the mass of metal evaporated and ρ its density, θ is the incidence angle, and r is the distance between the source and the deposition area. In terms of the vertical (h) and horizontal (δ) distances between the source and the target,

$$t = \frac{m'h}{4\pi\rho(h^2 + \delta^2)^{3/2}}, \quad (10)$$

or

$$t = \left[1 + (\delta/h)^2\right]^{-3/2} t_0, \quad (11)$$

where t_0 is the plating thickness obtained directly above the source at distance h ($\delta = \theta = 0$). In order to obtain uniform deposition from a point source, the target should lie on the surface of a sphere. The thickness is then equal to $m/4\pi\rho R^2$, where R is the radius of the sphere. In depositing from a capped crucible, the locus of the uniform deposition surface can be ovalized because of the directionality, or beaming, imposed by the crucible orifice.

To reduce crucible temperature and thus crucible-metal interaction, the metal can be heated directly by bombarding it with an electron beam, rather than indirectly by heating the crucible. A hot cathode, such as a tungsten filament, provides the electrons, and a magnetic field is used to direct the electron beam to the vapor-emitting surface. The highest temperature region is thus shifted from the crucible to the metal. In fact, the crucible can be cooled, or omitted completely by heating of a puddle in a block of the metal to be

evaporated, thus eliminating potential contamination from the crucible altogether.

To maximize the adhesion of the vaporized metal to the substrate, its surface should be free of oxides, grease, adsorbed water, or other contaminants. Heating the substrate usually enhances bonding, but reduces the deposition rate by re-evaporation of some of the plated metal. Ionization of the vaporized metal often helps surface adhesion. Ionization can be accomplished in an rf field or a plasma, usually a discharge in noble gases. In the plasma, only about 3% of the metal atoms are ionized, but the Argon ion bombardment of the substrate which results from the plasma which is formed by a discharge in Argon, increases metal adhesion by "hammering-in" the metal atoms. Unfortunately, entrapment of Argon in the metallized layer reduces its conductivity. Because an electric field is applied to the substrate when the vaporized atoms are ionized, the deposition thickness does not follow Knudsen's cosine law.

Another way to vaporize the source metal is to sputter it, which means bombard it with ions. The ions, usually produced in a glow discharge in Argon, are accelerated towards the metal, or target, with a voltage of about 500 volts. Sputtering of the metal occurs because of the transfer of momentum from the discharge gas. A threshold voltage (around 300-400 volts) is required to overcome the work function of the metal, before sputtering can set in. Above the threshold

voltage, the sputtering rate (Q) is directly proportional to the applied voltage (V) and inversely proportional to the pressure of the discharge gas (p) and the distance between the cathode and the target (d), or

$$Q = \frac{kV}{pd} \quad (12)$$

To maintain a constant sputtering rate, the gas flow rate must be adjusted to maintain a constant voltage and current density. In addition, the cathode temperature must be kept constant, since the current density increases with cathode temperature. The sputtering rate increases with the atomic weight of the discharge gas and decreases with the latent heat of evaporation of the target.

The sputtering efficiency, or the ratio of the latent heat of evaporation of the target to the impinging ion energy needed to vaporize one atom, is usually only 1%. Most of the excess energy is contained in the vaporized atoms which have about two orders of magnitude greater energy than thermally vaporized atoms. The greater energy of the sputtered atoms facilitates crystal formation of the deposited layers, within the practical limits imposed by re-evaporation. Since the sputtered atoms follow the cosine law, slightly modified by the collisions of the discharge gas and sputtered atoms, the target and substrate are usually arranged as planar surfaces parallel to each other, at a distance of approximately 5 cm, to achieve uniform deposition. As the center of the target is somewhat shaded

from the plasma by the substrate, the target is usually chosen about 50% larger than the substrate to attain sufficient sputtering.

2. Thick Film Screen Printing

Screen printing has been used for hundreds of years in printing fabric patterns and metal designs on china. It is a fairly simple process requiring only: (1) a screen to define the printed pattern; (2) a squeegee to transfer the "ink" from the top of the screen to the substrate; and (3) a fixture to hold the screen and substrate in their proper relative positions, while allowing movement of the squeegee. Downward pressure on the squeegee pushes the screen against the substrate and forces ink through the "open" parts of the pattern of the screen. The amount of ink that sticks to the substrate is a function of the screen's filament diameter and spacing, the emulsion thickness, the width of the line to be printed, the initial distance between the screen and substrate (snap-off distance), the viscosity and rheology of the ink, and the adherence of the ink to the substrate. If the ink cannot wet the substrate, then printing will be negligible. The ink used in screen printing of solar cells generally consists of: a metal powder (silver) with 5-10 μm diameter grain size; an organic vehicle composed of a solvent, such as butyl carbitol, and a binder (ethyl cellulose); and a frit, which could be a glass such as lead borosilicate. Recently, experiments have been performed replacing the frit by a flux, such as AgPO_3 .

The screen may be either a mesh of wire or nylon fibers, with the grid line pattern defined by use of an emulsion which closes the pores in the mesh in desirable areas, to prevent ink flow there, or an etched metal screen. The greater flexibility of the nylon screen is a disadvantage to resolution, because of its larger snap-off distance. The etched metal screen has very good resolution and a small snap-off distance, but is more expensive. Similar results can often be obtained with a cheaper, fine wire mesh screen. A 325 wire mesh can yield lines as narrow as 125 μm , although 175-200 μm line width is still more commonly considered as the practical limit of the present technology for a reliable process with acceptable yield. It is expected that this limit can be pushed to 125 μm in the future. The thickness for the printed lines is limited to about 25 μm before firing. The limit arises from adherence of the ink to the sides of the emulsion on the mesh.

After application of the ink, the printed parts are dried and then sintered, both in the air. The drying and sintering shrinks the ink volume by 20 to 50%. When sintered, the silver inks have an open matrix structure with a solid fill factor between 50 and 60%. The conductivity of the printed and sintered silver lines is at most 60% of the bulk conductivity for equal metal mass in the line, due to the limited area contacts between the silver grains.

A screen will last for about 10,000 cycles, a squeegee for a tenth of that. The squeegees need to be hard enough to

retain a sharp edge, yet soft enough not to unduly wear out the screen. The repetitive application of simple operations in screen printing lends this process readily to automation.

III. Comparative Evaluation of the Metal Deposition Options

A. General

In this effort, the attributes of the various applicable metal deposition options will be compared against each other. Such a comparison of the deposition options alone is only a first step in a comparative evaluation of the metallization process options, since the complete metallization process consists of a sequence of several steps - such as surface preparation, masking, pattern definition, conduction layer build-up, removal of mask, sintering, etc. The options for the complete metallization process thus form a submatrix to the matrix of the solar cell process options. In this submatrix, the number of process steps varies between options, as well as the interfaces to the main process matrix.

As an example, the various plating processes require the additional steps of masking, further conduction layer build-up, and mask removal, which are all not needed in thick film printing of silver. This process, however, requires a relatively high temperature sintering step to reduce contact and conductor resistance to acceptable values, which is usually not needed for plating. Also, some processes require some additional operations. For instance, in vacuum evaporation, the commonly used contact mask gets covered with deposition metal and must be periodically removed for cleaning. In the interface area, the suitability of some processes depends on preceding processes or the cell structure chosen. As an example, it seems not advisable to screen

print on texture etched cells due to potential damage to the peaks from the pressure of the squeegee. Even worse, some of the process steps in the metallization submatrix may be combined with process steps in the main matrix, such as AR-coating. For wet chemical plating options, for instance, a dielectric mask is required to define the metal pattern. But, since there is no metal deposit on the mask itself, the mask does not have to be removed if it can serve as, or complement, the AR-coating.

The various metallization options also result in differing conductor attributes, such as conductivity and minimum line width. These attributes determine not only the design of the solar cell, but also its ultimate performance. On large area cells, to achieve high performance, the front metal pattern should have a grid line width of 25 μm or less. This is well beyond the projected capabilities of some processes (e.g. thick film screen printing), and depends on the mask attributes for others (wet chemical plating and vacuum evaporation). The thickness of the metal layer also has a practical upper limit, which has, in generality, been taken as 10 μm for the lines of 25 μm or greater width, and as 40% of the line width for narrower lines.

Postponing these complications to a later point in the evaluations, the following discussion will, as a first step, examine the metal deposition only.

Some of the metal deposition options represent, by themselves, a variety of sub-matrices. For instance, for the electroless Ni plating process, several variations of surface preparation have been explored with conflicting results. They include nickel deposition on: bare, HF-dipped wafers; a Pd-layer applied by immersion plating; a Pd-layer applied by immersion plating, and built up electrolessly; a thin (50-100 Å) gold layer. The type of strike surface used determines the sintering conditions to be applied to the Ni layer. A few general requirements have emerged from the theoretical study of the influence of metallization design on solar cell performance. Foremost among these is that, to simultaneously minimize the losses from series resistance and from surface area coverage which causes current loss from shadowing, the sheet resistance of the grid line needs to be as low as possible. This requires high metal conductivity and large thickness. The use of copper with its high conductivity, second only to silver, is therefore indicated. It is further imperative that the deposition process yields a layer of bulk conductivity, and not only about one third of it, as the powder deposition and sintering processes do.

According to their general nature, outlined in the preceding section, the discussion of the metallization options will deal with them as four major groups: the wet chemical plating, which includes immersion, electroless, and electrolytic plating; vacuum deposition, including

Table IA

Metallization Process Options

Process	Applicable Metals	Coating Thickness (um)	Purpose of Coating	Typical Sintering Requirements	Major Steps	Remarks
Electroless Plating	Ni on Si	0.5	Pattern for chief Cond. or barrier	300°C; 30 min	HF dip, plate, rinse and dry, sinter.	Adherence to Si and contact resistance is variable
	"	5	Chief cond.	Optional	Plate, rinse and dry.	-
	Ni on Pd	0.5	Pattern for chief cond. & or barrier	None	Plate, rinse and dry.	-
	"	5	Chief Cond.			
	Ni on Au	0.5	Pattern for chief cond.	None	Plate, rinse & dry.	Shouldn't be exposed to high temperatures (>300°C)
	Pd on Si or on Pd ₂ Si	0.01	Ohmic contact and barrier against Ni	300°C; 15 min in N ₂	HF dip, plate, rinse and dry, sinter,	Forms Pd ₂ Si when sintered
Immersion Plating	Cu on Ni	5	Chief cond.	None	Plate, rinse, and dry.	Only recently has solution stability been acceptable.
	Pd on Si	0.01	Ohmic contact and barrier against Ni	300°C; 30 min in N ₂	HF dip, plate, rinse & dry, sinter, hi-pressure scrub, HF dip, plate.	Forms Pd ₂ Si when sintered

Table IA (Continued)

Metallization Process Options						
Process	Applicable Metals	Coating Thickness (μm)	Purpose of Coating	Typical Sintering Requirements	Major Steps	Remarks
Electroless Immersion Plating	Au on Si	0.002	Strike layer	None	HF dip, plate	Shouldn't be exposed to high temperature ($>300^\circ\text{C}$)
Electrolytic Plating	Cu on Ni	8-10	Chief Cond. layer	None	Plate, rinse & dry.	Must avoid direct Cu-Si contact.
"	Ni on Si_2	8-10	Chief Cond.	300°C ; 30 min in N_2	HF dip, plate, rinse & dry, sinter	Need organics in plating solution.
"	Ag on Ni	5	Chief Cond.	None	Plate, rinse and dry.	Current density between 10-20 mA/cm^2

resistance and electron beam heating as well as sputtering and ion plating; thick film screen printing; and deposition from the melt, such as solder dipping, which is at times used for conduction layer build-up. The processing parameters for each metal deposition option are considerably affected by the type of metal applied. An extreme case in this respect is the thick film process, where it has been found practically necessary to work with noble metals (e.g. silver) to avoid oxidation of the metal powder in the binder burn-off step. However, the high cost of the noble metals, including gold, silver, palladium, will severely limit their use in the manufacture of solar cells and modules for large scale terrestrial application. As a consequence, grid patterns of base metals are preferred, but their successful application by thick film methods requires further development. The wet chemical plating options appear not to be the most appropriate for applying base metal grids; the operating conditions lead to a reduction of the grid metal. Even though oxidation of the substrate or silicon surface might seem to be a problem in wet chemical plating, the thickness of the silica layer covering the silicon may be reduced when exposed to the plating solution, at least in electroless nickel plating, as recent studies have shown⁽¹⁾.

A summary of the metal deposition process options, used or being considered for low-cost silicon solar cells, is contained in Tables IA-IC. In these tables, the normally applied

metal thickness (which determines the function of the metal layer), the metals, to which the process is normally applied, and the major processing steps are listed. The Midfilm process has been listed separately in these tables, as it represents a cross between a photolithographic and a thick film process.

B. Chemical Deposition Processes.

1. Electroless Plating.

The first set of options listed in Table IA refers to electroless plating which is now mostly used to apply only a thin layer (up to $\sim 5000 \text{ \AA}$) as a pattern for further conductor build-up. Electrolytic plating, just as the older method of solder dipping, is primarily used for this further conductor build-up. If copper is applied as the main conductor, then a "barrier layer" is needed to prevent copper penetration into the silicon wafer. Nickel has been found to provide an effective barrier against copper diffusion, and it is convenient that it can be applied by electroless plating.

In electroless nickel plating, the nickel is deposited by the chemical reactions described by reac (5) and (6) in the preceding section. Approximately three moles of hypophosphite anions are consumed for each mole of plated nickel due to two side reactions. One is the break-up of the hypophosphite anion into H_2O , OH^- , and phosphorus caused by reaction with the adsorbed hydrogen atoms, such as:

The other side reaction is the evolution of gaseous hydrogen, instead of adsorbed hydrogen, from the reactants in reac (5). This reaction is:

There is still some debate over the type of surface which nickel can be most advantageously applied on. By the three organizations examining electroless nickel plating under the JPL/LSA project, three different procedures were used. Before applying the nickel layer, Motorola covers the grid pattern with a Pd-layer, applied by immersion plating and in some cases built up further with electroless plating. Photowatt applies the nickel layer over a thin gold layer which is formed by immersion plating, while Solarex deposits the nickel directly on the silicon surface by electroless plating. It is to be noted, that the surface preparation prior to the metal deposition process has a major influence on the success of the plating process. First, the electrical conductivity of the semiconductor plays a role, with the more heavily doped materials being easier to plate. Second, the mechanical surface structure has a significant influence, with the coarser surfaces (sandblasted, coarsely lapped) resulting in better adhesion. And finally, the chemical cleaning processes used immediately prior to plating, including an HF dip with or without subsequent short rinse, are recognized as important steps in a successful plating process.

The electroless nickel plating options are listed in Table IA. Even though the electroless application of a bulk nickel conductor is shown in Table IA, it is now more commonly proposed that the nickel be used only as a thin layer, as the brittleness of the electrolessly plated layer (due to the presence of phosphorus in the Ni deposit) causes thicker layers to peel relatively easily from the silicon during temperature cycling.

With proper care of the electroless nickel plating solution, by cleaning the wafers of particulates possibly carried into the bath and by filtering out precipitates to avoid having the solution plate out on itself, and by adding a replenisher solution which contains NH_4OH to maintain the proper pH and NiCl_2 to replace the plated-out nickel, the solution lifetime can be quite extensive. In current cost studies for electroless plating of nickel, it is assumed that one liter of solution could effectively plate, without replenishment, 34 m^2 of polished cells with 5% front area coverage to a layer thickness of $5,000 \text{ \AA}$. It may be noted, that the high mobility of nickel cations in the solution allows the indiscriminate plating of textured surfaces, which, because of the greater surface area of the texture etched cells, decreases the capacity of the plating solution. The nickel plating solution consists of 2.5 wt% $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 5 wt% NH_4OH , 1 wt% $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 4 wt% NH_4Cl , 7 wt% $\text{Na}_2\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 80 wt% H_2O . The $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is the

metal source, the ammonium hydroxide and the ammonium chloride maintain the pH of the solution, the sodium citrate is a chelating agent, and the sodium hypophosphite is the reducing agent for the nickel. Increasing the pH might increase the rate of production of adsorbed hydrogen atoms and plated nickel (reac (5) and (6)), but it also increases the rate of a conflicting reaction (reac (14)). Raising the temperature of the plating solution increases the plating rate, but the stability of the plating solution decreases. A solution temperature of 90°-95° C gives acceptable plating rates and solution stability. It would first be expected that the plating rate could be increased by using more sodium hypophosphite than listed above. However, too much sodium hypophosphite decreases the stability of the solution, so that it could plate anywhere, not just on the silicon or cleaned metal surface. The ammonium chloride acts as a buffer and aids in maintaining the solution pH since it is a salt of the weak base NH_4OH . The complexing agent sodium citrate helps to keep solution particles and metal ions in solution. Solid particles not only cause a rough deposition, but can also act as catalytic nuclei that lead to solution decomposition. The electroless plated nickel layer generally shows good uniformity, with few pores and a fine crystalline structure. Part of this is due to the presence of between 3 and 15 wt% phosphorus in the nickel layer due to reac (2). The phosphorus gives the nickel layer a high corrosion resistance,

but also brittleness compared to a pure nickel layer. The resistivity of the Ni-P layer is about an order of magnitude higher than that for pure nickel - $60 \mu\Omega \text{ cm}$ compared to $6.35 \mu\Omega \text{ cm}$. As the electroless plated nickel layer normally serves a sentizing function, its high resistivity does not form a handicap. However, the diffusion of phosphorus from the nickel layer into the wafer can electrically influence an underlying p or p^+ layer. Also, care must be exercised in heating the electroless nickel layer, since the compound Ni_3P is formed at about 400° C . The nickel phosphide affects the hardness of the metal layer due to crystallite growth.

Both the adherance of the electroless nickel layer and the unit area contact resistance (desired to be $\leq 10^{-4} \text{ ohm}\cdot\text{cm}^2$) are dependent on the nature of the substrate and on sintering temperature and time. Although nickel can be (and has been in production quantities!) successfully plated electroless directly on silicon, and even without sintering, its adherance and contact resistance have been found to be difficult to control. The former could be due to variations of the nickel layer thickness. The brittleness and thermal expansion coefficient mismatch between the nickel and silicon become more apparent, as the thickness of the layer increases. In one series of experiments⁽²⁾ it was found that $5000 \text{ \AA}$ thick layers adhered well to silicon, while $10,000 \text{ \AA}$ layers separated easily. The silica layer thickness also affects adherance and contact resistance. If the silica layer is

too thick ($> 50 \text{ \AA}$) to readily permit tunneling, then it will act as a dielectric layer, and electroless plating will not occur. If there is no silica present on the silicon surface, then a displacement reaction will occur with the plating solution between the nickel and silicon, due to the high reactivity of silicon. This is thought to create a porous interface layer between the silicon and the nickel, and thus to decrease the adherence of the deposits.

It has been shown recently⁽¹⁾ that the silica layer thickness decreases in the electroless nickel bath, and that the plating does not actually commence until the silica layer thickness has been adequately reduced, i.e. to near $50 \text{ \AA}$ to allow a sufficient amount of electron tunneling. This decrease of the silica layer thickness could result from a reduction of the silica by the ammonium hydroxide, and its dissolution by complexing with the sodium citrate in the solution. Since different silica thicknesses thus would require different processing times, it would be desirable to maintain a standardized silica layer thickness in a production line situation. This might be accomplished with a dilute HF dip immediately prior to the electroless plate. Processing times and temperatures for depositing $5000 \text{ \AA}$ of Ni on "bare" silicon are 5 to 6 min at 80 to 90° C .

To form an ohmic contact on non-degenerate silicon, i.e. not heavily doped and/or sandblasted silicon, the nickel layer has to be sintered after plating, which is thought to

result in the formation of Ni_2Si . The sintering temperature has to be kept low, to minimize the formation of Ni_3P in the metal layer and the diffusion of nickel into the silicon wafer. Nickel atoms in the depletion region can lower the cell efficiency through the formation of recombination centers, while nickel aggregates can even short out the junction. The sintering conditions for electroless deposited nickel are therefore usually 300°C for 30 min in an inert atmosphere. On cells which are solder dipped, a separate sintering step is usually not performed. It is possible that the short heat cycle connected with the solder dipping operation is adequate for the Ni_2Si formation.

To shield the wafer against nickel penetration, and to ensure contact adherence as well as coherence, a palladium layer is sometimes electroless deposited prior to the nickel plating, in a "sensitizing bath". The palladium forms a barrier against nickel penetration, and it presents a very active surface for the adsorption of hydrogen atoms. The palladium layer is usually sintered for 30 min at 300° in a nitrogen atmosphere to establish an ohmic contact by the formation of palladium silicide. No additional sintering is then needed after deposition of the nickel layer. A gold strike layer, approximately $20\text{ \AA}$ thick, can be deposited in lieu of the Pd layer prior to the nickel plating. The role of this gold layer is not well understood. It probably does not act as a barrier to nickel penetration, and gold itself

penetrates readily into silicon and forms recombination centers there. However, the presence of a gold layer aids in providing an adherent and ohmic nickel layer without the need for sintering. The absence of a sintering step in the Au-Ni layer minimizes the metal penetration problem during the solar cell fabrication process. In one reported sequence, the gold layer is plated by immersion of the wafers for 30 seconds into a basic electroless solution which contains 0.2 wt% potassium cyanaurate as the gold source, 6.6 wt% ammonium chloride, 4.4 wt% sodium citrate, and 1 wt% sodium hypophosphite. These chemical constituents serve the same purposes as they do in the electroless Ni plating solution. The solution is maintained at a pH between 7 and 7.5 by addition of ammonium hydroxide. It has been found that the addition of 1 wt% HF to the electroless gold solution reduces its best operating temperature from the 90°-95° C range to room temperature. Whether the HF increases reactivity of the solution or of the surface, is not known. It could also be that it is simpler to precisely control the thickness of the thin gold layer by keeping the gold solution at room temperature where its reactivity is lower. Just prior to exposure to the gold plating solution, the wafers are dipped in concentrated HF (48 wt%) for 30 seconds. After the gold layer is applied, the wafers are rinsed thoroughly with DI H₂O for 5 minutes before being electroless nickel plated.

In another process sequence, palladium is applied via

immersion plating and then built up with electroless plating prior to the electroless nickel plate. The immersion Pd-layer is about 50 Å thick, while the electroless layer is 1000 Å thick. The palladium immersion solution contains PdCl_2 as the Pd-source, HCl to help dissolve the PdCl_2 , and NH_4F to complex with the silicon cations by formation of fluorides. Control of the immersion reaction rate is important; too rapid a rate leads to non-adherent or spongy deposits. The silica layer thickness is minimized by dipping the wafers in a 1 wt% HF solution just prior to plating.

In the Motorola process sequence, the immersion plating, which takes 5 min, is done twice, with DI H_2O rinses, a short aqua regia dip (5 sec), and a 20 sec 1 wt% HF dip between the immersion plating steps. After the second plating operation, the cells are rinsed with DI H_2O , dried, and sintered for 15 min at 300°C in a nitrogen atmosphere. The palladium layer is then built up by electroless Pd plating. The composition of the electroless Pd-solution is very similar to that for the nickel solution, save that PdCl_2 is the metal source. The cells are placed for 45 sec in the electroless Pd-solution which is kept at 50°C and a pH of 9.7. The cells are then rinsed with DI H_2O , dried, and sintered at 300°C for 30 min in a N_2 atmosphere. It might not be necessary to have such a thick Pd-layer prior to the nickel plating. More recently, Motorola has been able to fabricate good cells by electroless plating nickel over an immersion Pd-layer. Sintering is then done only after the nickel is plated.

2. Electrolytic Plating.

Electrolytic plating is considered in solar cell fabrication primarily for the deposition of copper for the purpose of conduction layer build-up. The most common solution used for plating copper is an acid which consists of approximately 150 to 200g of copper sulfate ($\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$) and 30g of concentrated sulfuric acid in a liter of water. The copper sulfate transports the copper from the anode to the cathode. But because only about 25% of the CuSO_4 is ionized in an aqueous solution, the conductivity of a CuSO_4 solution is low. Therefore, one of the chief purposes of the sulfuric acid is to increase the conductivity of the electrolytic solution. The conductivity of a 1 n H_2SO_4 is about 6 times larger than that of an equivalent CuSO_4 solution - $0.200 \text{ mho cm}^{-1}$ compared to $0.035 \text{ mho cm}^{-1}$. In addition, the sulfuric acid promotes anode reduction by reacting with it, and further, by attacking copper aggregates, the sulfuric acid fosters a smooth deposition. Colloidal particles, such as starches, in the electrolytic solution also promote smooth deposition by accumulating at the high points of the wafer. Since the high points of the substrate are closer to the anode, heavier deposition is normally experienced there. However, an excessive deposition on high points is reduced by the presence of colloids. Also required for smooth deposits is good wetting of the substrate or cathode surface, since beading of the electrolyte would concentrate deposition into selected areas.

During the electroplating, the solution is kept at a moderately high temperature ($\sim 50^{\circ}\text{C}$) since the conductivity of the solution increases with temperature. However, the stability of the electrolytic solution sets an upper limit to its operating temperature. Also, the solution has to be agitated during plating, to redistribute the ions and prevent charge accumulation at the electrodes. Further, the electrolytic solution should be constantly filtered through diatomaceous earth to rid it from particulates. The filtering rate should be fast enough to turn over the electrolytic solution once an hour. The accumulation of precipitates, or solid particles, would affect the coherence of the deposition. Since the grid lines are only 5-10 μm thick and 40-120 μm wide, the inclusion of particulates in the grid pattern could be detrimental to the grid line integrity. Another technique, besides filtering, to minimize deposition of solid particles, is to place bags around the electrodes. One suggestion ⁽³⁾ is to use a 10-12 oz. cotton flannel inner bag with a napped polypropylene outer bag.

Unlike electroless and immersion plating, which could be done in a simple flow tank with a recirculating system, electrolytic plating requires fairly large plating tanks. These tanks have to be electrically insulated towards the solution and are therefore normally made of steel with a rubber lining, such as Koroseal from Goodyear. Before a new tank can be used for plating, the tank has to be leached with a

weak alkali solution to remove any loose organics. In order to plate 2400 solar cells of 10 cm x 10 cm size per hour, assuming a cycle time of 5 minutes for the plating operation, two tanks would be required, each of approximately 185 cm x 215 cm surface area and of adequate depth to accommodate one cell placed vertically. In this setup, the tank would contain six anodes parallel to each other along the long side of the tank, placed 30 cm apart. Equidistant from the anodes and the tank walls are five cathode racks, each rack containing 20 wafers, being plated on both sides simultaneously. A plating current density of 60 mA/cm^2 will give a coating thickness of about 6 μm in 5 min using the acid plating solution.⁽⁴⁾ In this scheme, it is assumed that an electrical connection can be made to each of the 100 wafers that are in a tank simultaneously. This would require loading and unloading 10 racks with 20 wafers each every 5 minutes, probably by automatic means. It may be noted that the plating current amounts to 6 A per solar cell, or 600 A per tank. It is also to be observed that the tank can be made deeper, and thus accommodate a multiple of the 100 cells per load discussed. This can be used to eliminate the second tank and/or increase plating time or throughput.

For plating copper directly on a nickel grid pattern, the acid bath solution may not be desirable because of the possible displacement reaction between copper ions and nickel metal. The displacement reaction, which occurs because

nickel is more reactive than copper, would result in incoherent deposits. To avoid this reaction, wafers with an electroless nickel coating, could, prior to copper plating, be dipped in an alkaline "coppering" solution. This solution both cleans the surface and deposits, by immersion plating, a thin layer of copper on the nickel surface. The coppering solution is composed of: 50 g of NaOH, to emulsify oil; 50 g NaCN, for complexing metal ions; 50 g of Na_2CO_3 , to give the proper pH; and 25 g of CuCN, as the source of copper; and one liter of water. The cyanide complexes with the copper cation, effectively decreasing the copper activity.

Another common electrolytic plating method, which does not require a preceding "coppering" bath, utilizes a copper cyanide plating solution. This solution contains Rochelle Salt ($\text{NaKC}_6\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) which is also a complexing agent, copper cyanide, sodium cyanide, sodium carbonate, and sodium hydroxide. Sodium cyanide complexes with copper as follows:

The desired operating pH of the Rochelle salt solution is 12.6, which is adjusted by the addition of NaOH or H_2SO_4 , depending whether it is desired to raise or lower the pH. The operating temperature of this solution is between 50° and 90° C, and current densities used are between 20 mA/cm^2

and 50 mA/cm². Besides being able to plate active metals without a displacement reaction, electrolytic solutions containing cyanide have good throwing power, or the ability to produce even deposits on irregular surfaces. The throwing power of the cyanide containing solution is about five times larger than that of the CuSO₄ - H₂SO₄ solution.

It has also been proposed to electroplate nickel grid patterns directly on the silicon wafers. It is undesirable to plate copper directly on silicon because of the detrimental results on cell performance of copper penetration into the silicon. The lower conductivity of nickel would require that its plating thickness be about four times larger than that for copper, which, however, may not be practical. The equipment and procedures for nickel plating are similar to that for copper plating, except, of course, for the difference in electrolytic solution and the anode material. To prevent rough deposits, the nickel anodes should be double bagged. One liter of nickel electrolytic solution consists commonly of 327 g of nickel sulfamate (Ni(SO₃NH₂)₂), as the nickel carrier, and 30 g of boric acid which acts as a buffer. There are also traces of chemicals added to increase the anode reactivity and the deposition smoothness. Since pure nickel is a fairly inactive anode, a sulfur depolarized nickel anode is used. The optimum operating conditions for the nickel sulfamate solution are a temperature of 49° C,

a pH of 4.0, a current density of 60 mA/m^2 , and a voltage between 4 and 8 volts (DC). Approximately 1 ml of nickel replenisher solution should be added for every ampere-hour of charge passed through the tank.

C. Thick Film Screen Printing

Screen printing appears to be a very simple process for applying the bulk conducting layer on a solar cell. The application of the conductor in the desired pattern is essentially a one-step operation using a screen printer, requiring neither prior pattern definition nor further conduction layer build-up. The pattern is defined by a wire mesh or metal screen which can be re-used about 10,000 times. However, the currently available thick film procedures are incompatible with the requirements of a low-cost solar cell production line. For one, the only metal that can be practically used for applying contacts to silicon solar cells by screen printing is silver, primarily because of the need for burning off the binder in the ink before sintering the layer. This burning-off of the organic material requires oxygen, which, at the same time, would cause oxidation of the metal particles in the ink, were they of non-noble metals. In the quantities required, silver is too expensive to permit meeting the price goals for the modules. Secondly, the conductance of a layer of screen printed and sintered silver, containing an equal mass of metal as a bulk layer of the same metal,

Table IB
Metallization Process Options

Process	Applicable Metals	Coating Thickness (um)	Purpose of Coating	Typical Sintering Requirements	Major Steps	Remarks
Thick Film Screen Printing	Ag on Si	12	Chief Cond.	125°C; 15 min for drying followed by 675°-700°C; 90-120 sec.	Screening, sintering	Gridline density is 50-60% of bulk; line width 250 um; Polished surfaces preferred.
"	Sn:MoO ₃ (75:25) on Si	15	Pattern for chief cond. (solder)	400°C; 5 min to burn out C, followed by 700°C for 30 min in N ₂ and H ₂ mixture	Screening, sintering	Small quantities of Ti (20 ppm) decreases contact resistance. Polished surfaces preferred
"	Cu on Si	10-15	back contact only	550°C, 5 min in N ₂ for adherence followed by 590°C for 8 min in N ₂	Screening, sintering	Cu paste contains AgF ₂ to act as a flux and Al-Si eutectic to promote ohmic contact
"	Al on Si	15	back surface field	850°C, 20 sec	Screening, sintering, removal of excess Al	Al-Si eutectic formed during sintering which results in a high conc. of Al in the Si.

is only about half that of the bulk silver layer, due to the limited contact area between adjacent grains in the sintered layer. Therefore, twice as much metal has to be placed on the wafer in a screen printed layer than in a wet chemical or vacuum deposition process. In addition, as the screen printed and sintered lines contain a lot of voids, with a density factor between 40% and 60% of bulk density (see Table IB), about four times the volume of a bulk metal line is needed for equal conductance. However, the thickness of a screen printed and sintered layer is limited to approximately 20 μm for a single screen printing. A second layer could be applied after sintering the first layer, but this would involve pattern registration and would appear to be even more uneconomical. Thus, a single screen printed layer is equivalent in performance to a 5 μm thick plated layer. Thirdly, the line width in screen printing is, today, still practically limited to 175 to 250 μm minimum, with about 125 μm projected for the future. This limitation causes more shadowing of the cells than experienced by other deposition processes which are capable of smaller line width.

The composition of the screen printing ink usually includes the following: metal particles with a mean diameter of approximately 5 μm ; a glass frit to foster metal flow and adherence during sintering (a common type is the Drakenfeld frit which is a lead borosilicate glass $\text{PbO}:\text{B}_2\text{O}_3:\text{SiO}_2$ in the mixture 80:10:10 (wt%)); a binder, such as triethyl cellulose,

to hold the ink together; and a solvent, such as trichloroethylene or butyl carbitol, to give the ink the correct viscosity. After the ink is applied with a screen printer, it is dried at approximately 125°C for 5-15 min to evaporate the solvent, and then sintered at approximately 700°C for a minute or two, to coalesce the metal particles to each other and to the surface of the wafer. An automatic screen printing machine is projected to print up to 2400 10 cm x 10 cm wafers an hour with a line resolution of 125 μm , using 325 mesh wire screen. A metal screen could print lines with about 50% higher precision than a wire screen, but is considerably more expensive. The function of the screen printing machine is to firmly hold the silicon wafer and screen in fixed position relative to each other, with a close and uniform spacing between them, apply a fixed amount of ink, and to move the squeegee over the screen in order to push the ink through the screen onto the wafer's surface. During the printing or "striking" step, the screen is pushed into contact with the wafer by the squeegee. After the squeegee has passed, the screen "snaps-off" from the wafer, imparting a large sheer force to the ink, and thus hardening it so it can retain its shape. As mentioned earlier, the grid pattern's uniformity and quality is affected by the speed, pressure, and attack angle of the squeegee (angle that the squeegee makes with the screen), and the snap-off (substrate-to-screen) distance. Typical conditions are a squeegee speed of 8.4 cm/sec with

an attack angle of 45° , and a snap-off distance of $0.064 \text{ cm}^{(5)}$. Since the snap-off distance should be constant over the wafer's surface, and because the squeegee exerts a significant downward force on the wafer, it might be difficult to print warped wafers with acceptable yield. The squeegee speed affects the flow properties of the ink. Normally, silver screen printed inks are thixotropic, i.e. they exhibit a hysteresis, which means a finite recovery period after snap-off. A thixotropic ink, as opposed to a pseudoplastic one, will retain its low viscosity for a short time after snap-off.

The ratio of the printed ink's line thickness to width decreases with increasing line width, since relatively more ink sticks to the screen for thinner lines. For $125 \text{ }\mu\text{m}$ wide lines, the largest wet ink thickness may be about $20 \text{ }\mu\text{m}$, which results in 10 to $16 \text{ }\mu\text{m}$ thickness of the sintered line. This, coupled with the relatively low conductance of the screen-printed lines means, that larger series resistance connected losses will have to be accepted, if screen-printed lines are selected over some other metallization process options.

The current cost of screen-printing silver is dominated by the cost of the silver ink, which in turn is determined by the silver price. A silver price of $\$0.40/\text{g}$ ($\sim \$12.50/\text{troy oz}$) has been assumed for these calculations. With a price of $\$0.30/\text{g}$ for the glass frit, binders, solvents, and formulation, the total ink price will be $\$0.70/\text{g}$. The process details included in Table I were obtained from "Format A"

information supplied by the respective organizations. In some cases, the process data given were not complete, e.g. screen and squeegee costs were left out.

In order to fit thick film screen printing into the LSA framework, the screening of base metals is being explored. The two principal examples of this effort are the screen printing of an ink based on a mixture of Sn and MoO_3 powder, and one of copper using a AgF flux. (Table IB). The last process has been used primarily for the formation of the back contact. The thick film application of aluminum to the back surface will not be discussed in this context, since it is applied primarily to form a heavily doped p^+ layer and a high-low junction by the alloy-regrowth process, and usually requires further conduction layer build-up.

The tin:molybdenum oxide screening is a primary step to define the grid for conduction layer build-up by solder dipping.⁽⁶⁾ The ink solids consist of a 3:1 wt ratio of Sn to MoO_3 , with one part in 50,000 of TiSi_2 added. The titanium silicide is supposed to lower the contact resistance. The ink solids are used in a vehicle which is composed of 75 wt% solvent, e.g. trichlorethylene, and 25 wt% binder, e.g. ethyl cellulose. Two parts of powder are used with one part liquid. After the Sn: MoO_3 ink is applied to the wafer by screen printing, the wafer is air dried, heated to 400°C in air to burn-out the carbon, and then sintered at 700°C for half-an-hour in a reducing atmosphere consisting of

hydrogen (40%) and nitrogen (60%). After cool-down, the wafers can be solder dipped.

The application of copper ink using a AgF flux is still in the experimental stage.⁽⁷⁾ The AgF which composes about 2 wt% of the ink, melts at 435°C and dissociates at 460°C, with the nascent fluorine reacting with the silicon dioxide and reducing the silica layer thickness. After the Cu:AgF ink is applied by screen printing, it is activated by firing for 5 min at 500°C in nitrogen atmosphere, and then sintered for 8 min in a hydrogen atmosphere at 550°C. The first firing establishes the adherence of the metal to the silicon, the second the bonding of the copper particles to each other. The process does not involve any organic binder which would need to be burnt off, nor any oxide containing flux. Thus, the process can be carried out in an oxygen-free environment and therefore be applied to base metals such as copper. It is still subject to the other limitations of the thick film processes, and it involves handling of the quite costly AgF in a completely dry atmosphere, since it decomposes with very small amounts of moisture.

Currently, adherent and coherent copper contacts have been made to silicon with apparently little cell degradation from copper contamination. Using copper inks, doped with aluminum germanium or aluminum silicon eutectics, to form the back contacts, bare cells with efficiencies of 9.4% have been produced.⁽⁸⁾

Table IC
Metallization Process Options
c. Other Options

Process	Applicable Metals	Coating Thickness	Purpose of Coating	Typical Sintering Requirements	Major Steps	Remarks
Midfilm	Ag on Si	8.5	Chief Cond.	650°C, 60-100 sec; 700°C, 30-70 sec in air	Applying Midfilm, exposure, applying metal, sintering	Works best with spherical particles resolution about 50 um
"	Cu:Sn	Not available	-	700°C for 5 mm in N ₂	Same as above	Successfully fired on Si wafers only
Vaccuum deposition	Ti:Pd:Ag on Si	0.01:0.01:5	Bonding:barrier: Chief cond.	None	Load, evaporation unload	Used for space cells
	Ni:Cu on Ng	0.5:10	Barrier: chief cond.	None	Load, evaporation, unload	Modification of above procedure
Solder dipping	Sn:Pb (60:40) on Ni	>55	Chief cond.	None	Flux dip, solder dip, clean, rinse and dry	Must have metal pattern. Thicker on bus bars.

D. Vacuum Deposition.

Vacuum deposition also has been used in large scale manufacturing of various products. Although it often is reputed to be a high-cost process, it has been applied, for instance, for the mass production of metallized plastic parts for low-priced merchandise, such as toy cars. The process is also capable of automation, as the successful operation of several fully automated vacuum process lines for the low-cost deposition of precision four-layer optical interference coatings at OCLI (Santa Rosa, CA) shows.

One of the attributes of the process is that it has to be carried out in a controlled environment, namely in a high vacuum in the case of vacuum evaporation or ion plating, or a low pressure gas such as argon in the case of sputtering. This causes some complication for the loading and unloading of the work in process. In laboratory type and small production equipment, the chamber is opened to the atmosphere for unloading and loading. Subsequently, the chamber is closed and pumped down to the required vacuum level. This pump-down requires some time, often 15 to 30 minutes, during which the relatively capital intensive equipment, and often also its operator, are not productive. Installation of larger capacity pumps - an additional capital investment - can reduce this pump-down time to approximately 5 to 10 minutes. For mass production purposes, continuously operating conveyerized systems have been investigated about ten

years ago. These systems are always open at the loading and unloading sides, although the openings are restricted as far as possible. Thus, in front and behind the actual process chamber in which a high vacuum is continuously maintained, a sequence of pumps has been installed to achieve a suitable pressure gradient between the outside environment and the pressure in the process chamber. This approach requires large equipment and considerable energy consumption for the continuous maintenance of the pressure gradient. This equipment is therefore not considered economical, and is no longer produced. The alternative for mass production is a quasi-batch operation with air lock chambers for the loading and unloading of the work in process. These air locks are located between the ambient and the process chamber which, in this approach, is also continuously maintained at the high operating vacuum. For entry or exit of work in process, the air lock is opened to the ambient, while closed to the process chamber. The gate to the ambient is then closed vacuum tight, and the chamber pumped down to the pressure of the process chamber. Subsequently, the gate to the process chamber is opened to permit passage of the work in process between the air lock and the process chambers. After closing this gate again, the pressure in the air lock is raised to the ambient pressure, usually simply by admitting outside air. For large production systems, two air lock chambers are usually provided, to permit separate entry and exit

means for the work in process, and to permit a smoother material flow.

Energy is continuously consumed in vacuum deposition systems for the pumping to maintain the required pressure in the process chamber, and somewhat more intermittently for the pump-down in the air lock chambers. In addition, the substrates are sometimes electrically heated to an elevated temperature during the deposition process. Finally, energy is needed for heating and evaporating the material to be deposited. This heating is now frequently done by an electron beam.

The vacuum deposition process is a highly controllable process, both with respect to the quality of the deposited materials and to the layer thickness, as well as their uniformity. However, even in a high vacuum process (about 10^{-6} Torr) there are some residual gases in the process chamber, some originating from backstreaming of oil from the vacuum pumps. These gases can interact with the material to be deposited or enter into the deposited layer, somewhat modifying its properties. Through proper vacuum chamber construction and maintenance, however, this contamination problem can be adequately controlled. In the systems which are equipped with air locks, and where the process chamber is continuously maintained at the operating vacuum level, the possibilities for contamination are greatly reduced in comparison to those systems which are periodically opened to the atmosphere.

One of the major problems with vacuum deposition is that the material evaporated from the source does not deposit only on the desired areas. The evaporated material leaves the "source" on straight line trajectories and deposits on all surfaces in its path. While simple laboratory type sources deposit material into a hemisphere around the source, more sophisticated sources, or "boats", incorporate baffles and "chimneys" to restrict the exit angle and deposit material predominately in a cone which does not have to be significantly larger than that containing the work in process. Nevertheless, there is always some overspray, as well as material transport to gaps between individual pieces of the work in process, which results in a deposition of material on parts of the equipment. Thus, the equipment has to be opened periodically and partially torn down to permit removal of this unwanted deposit. It is noteworthy that about 75% of this spuriously deposited material can be reclaimed.

Patterns in the deposit can be readily defined by repeatably usable "shadow masks" which are positioned close to the work in process in the path of the evaporated material. An alternative is the application to the work in process of a temporary mask, a "resist", such as a photoresist. Where mechanical shadow masking is used, evaporated material will gradually build up on the mask, and will restrict its pattern openings. Thus, after a certain period of time, the mask has to be removed and cleaned, requiring

the expenditure of labor and chemicals. Again, about 50% of the material deposited on the mask can be reclaimed. As a result of these handling and cleaning operations, however, the mask life becomes limited.

In many applications, the source boats have to be brought periodically to rather elevated temperatures and cooled down again, which reduces their useful life. A further life limitation of the source boat is, at times, caused by interaction between the boat material and the material to be evaporated. Nevertheless, 1000 lbs of copper have been evaporated from one graphite source boat in a large production system. (9)

Vacuum evaporation has the following attributes which are beneficial for large scale solar cell production: a well controllable, automatic process, capable of yielding very fine line ($< 10 \mu\text{m}$) patterns, and of providing layers of bulk material properties, and capable of pattern generation with reusable masks. It has, however, also a number of undesirable attributes which include impracticality of simultaneous deposition on both sides of the wafer, thus essentially doubling the capital costs (9), material loss through overspray and deposition on the masks, which result in the need for cleaning masks and chamber, need for periodic replacement of masks, source boats, and pump oil, and considerable, though tolerable, energy consumption. These attributes tend to make the process more costly than some

of the wet chemical options.

These problems tend to make the process unsuitable for the deposition of thick, fine line patterns. When a pattern of 10 μm thick conductors of 25 μm line width, as found desirable in the pattern optimization studies, is to be produced, then the 10 μm deposit would tend to reduce the width of the openings in the mask so much as to require cleaning after each deposition on one wafer. This would drive the costs up intolerably. The alternative would be to use a disposable mask, a resist on the wafer. With the required small line width, the resist application may require photolithography, a process of higher, but probably tolerable costs. However, a 10 μm thick film has a significant lateral strength. This thickness may not be adequately reduced at the steps between masked and unmasked areas to permit separation of the deposited film there without significant weakening or even destruction of the bond between metal and semiconductor in the unmasked areas. Such separation is usually no problem on thin films, with perhaps up to a micrometer thickness. These problems would not occur for deposition on the back of the wafers without masking.

IV. Conclusions

In consequence of the analysis of the metallization pattern optimization, in the two preceding quarterly reports, and of the qualitative comparison of the attributes of the various metallization process options in this report, it has become apparent that the thick film methods cannot meet the resolution and low resistance requirements, and that the vacuum deposition methods can meet the basic resolution requirements, but incur masking problems at the large metal layer thickness considered ($\sim 10 \mu\text{m}$). The process is principally still tractable, but will become too expensive because of this problem. This leaves the wet chemical process as the most promising, at least for conduction layer build-up.

The quantitative economic evaluation of the metallization process options, already largely completed, still be contained in the next quarterly report.

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