# SOLAR CELL METALLIZATION: HISTORICAL PERSPECTIVE

WILLIAM E. TAYLOR
Technical Director
Photowatt International, Inc.
Tempe, AZ 85281

Collector grid design involves a compromise of the dimensions of junction depth, grid spacing and grid width (all of which should be small), and cost, which depends on the technology used and which determines the minimum grid width (Figure 1). As the grid width resolution becomes smaller, the other dimensions can be made smaller and cell performance will improve, but costs tend to be higher for technologies with fine line resolution capability.

1. Xj should be small:

    a. increases blue response which increases efficiency,
    BUT b. increases sheet rho, which increases $R_s$ and decreases efficiency.

2. For given sheet rho, reducing $s_g$ will:

    a. reduce $R_s$ (increase efficiency)
    BUT b. increase shaded area, decreasing efficiency.

3. For given $s_g$, reducing $W_g$ will:

    a. decrease shaded area (increase efficiency)
    BUT b. this is limited by technology and cost.

For space applications, metallization design is driven by the cost of lifting weight into orbit. Hence space cell technology uses shallow junctions with narrow gridlines at premium prices for high efficiency and high reliability. Metallization technology is evaporation or sputtering with shadow mask or photolithography for pattern definition.

For terrestrial applications, design is driven by cost. Hence terrestrial design compromises performance by using deeper junctions and wider grid lines spaced farther apart in order to achieve lower costs on a per peak watt basis. Current technology favors conductive screen printed inks or electroless nickel plating with pattern definition by screen printed resist.

Typical values of pertinent parameters for current commercial practice are shown in Figure 2.

Contact metallization must satisfy a number of functional criteria (Figure 3). The need to avoid junction degredation during processing and subsequent service life and to attain and maintain good adhesion are critical, and are strong determinants of the metallization system design and materials selection.

## SPACE CELL METALLIZATION TECHNOLOGY

The first solar cells had no front surface metallization. The diffused junction wrapped around the edge of the cell to the back, where contacts were made. This situation was improved on by deploying a grid of metallic conductors across the illuminated surface to collect the current near its origin. Metallization progressed in an evolutionary fashion (Figure 4) from electroless nickel through evaporated titanium-silver contacts, which were invented and patented by Marinaccio and Lepselter at Bell Laboratories, to passivated contacts having a thin layer of palladium under the silver to electrochemically passivate the titanium. Evaporated or printed aluminum is sometimes used to promote ohmicity of the back contact and reduce the titanium sinter temperature. The aluminum may be sintered to establish doping of the silicon surface layers (P plus back surface field).

The Ti-Pd-Ag contact system has become the standard qualified space cell metallization system against which alternatives are compared. Other transition metals are technically acceptable but have not been adopted for commercial practice. The preferred method of fabrication, evaporation through metal shadow masks, limits pattern and hence cell size. Need for large size cells in large space arrays is forcing the use of photolithographic technology for pattern definition.

## TERRESTIAL SOLAR CELL METALLIZATION: PLATED CONTACTS

Electroless nickel plated contacts offer several advantages (Figure 5). The erratic and unreliable adhesion of electroless nickel can be overcome by sintering the contact, whereby a nickel silicide compound is caused to be formed. The nickel-silicon system is complicated by the formation of several different silicides (Figure 6). Nickel atoms diffusing into the junction depletion region can act as recombination centers and degrade cell performance. Anderson and Peterson observed that with 30 minutes sinter time, junction shunting becomes evident at 350 degrees and catastrophic at 450.

Electroless nickel plated contacts have been modified to improve adhesion and ohmicity by introducing thin layers of gold or palladium deposited by displacement or autocatalytic methods (Figures 8 and 9). The thin palladium deposit is sintered at 600 degrees to form the disilicide. The subsequent electroless nickel deposit is further sintered at 300 degrees to ensure a stable reliable contact.

Nickel plated contacts have a high sheet resistance, commonly overcome by solder coating. Copper plating over the electroless nickel is a cost attractive alternative which has been investigated, but is not yet in commercial use. Grenon and co-workers predict that such systems will have greater than 20 year life for exposure of 6 hours per day at 135 degrees.

## TERRESTRIAL SOLAR CELL METALLIZATION: PRINTED CONTACTS

The use of screen printing for solar cell contact metallization, first described by Ralph in 1972, has been extensively developed and is now widely used for terrestrial solar cells. The original screen printed metallization used commercial fritted silver conductive inks, and this has continued to be the practice.

The use of a brief dip in dilute hydrofluoric acid, frequently resorted to as a means of improving cell performance, results in such undesirable effects as unstable cell performance and erratic adhesion, both of which degrade in humid environments. Good, stable curve shapes can be obtained by the use of short (spike) firing techniques. This is typically achieved by sintering temperatures of 600 to 700 degrees for 30 to 120 seconds in infrared furnace equipment.

Sintering is carried out in an oxidizing atmosphere which generates an oxide layer on the silicon to which the frit can bond. However, the frit, acting as a flux for the oxide can allow the oxidation process to continue and to penetrate the junction. This possibly explains the necessity for the spike firing and the effects of HF treatment. Silver can also migrate to the junction by diffusion, resulting in degredation of cell performance. Junction depths of 0.35 to 0.5 microns are necessary to ensure long service life.

In the area of new developments, procedures to overprint and fire through $TiO_x$ AR coating have been described by Frisson. In the search for base metal systems, promising developments with molybdenum-tin have been reported by SOLOS and Spectrolab and with fritless copper inks by Ross.

## TERRESTRIAL SOLAR CELL METALLIZATION: BACK CONTACTS

Back contacts are more difficult to establish because of the tendency to form Shottky barriers. The formation of a more heavily doped layer by boron diffusion or aluminum alloying is advantageous. Both evaporated and printed aluminum have been used to form the P+ doped layer on the back surface. The aluminum must be sintered above the silicon-aluminum eutectic (577 deg. C) in order to provide the desired aluminum doped regrowth layer (Figure 11) which should be of the order of 1 micron thick. In the case of printed aluminum backs the use of a very short (spike) firing cycle at about 900 drgrees has been effective. Overcoating with evaporated Ti-Pd-Ag, by electroless nickel plating or tin-zinc eutectic alloy applied by ultrasonic soldering iron technique have been used to form solderable pads on printed aluminum backs. Alternatively, the printed aluminum may be stripped and replaced with a printed silver contact in a gridded configuration.

Figure 1. Solar-Cell Collector Grid Metallization

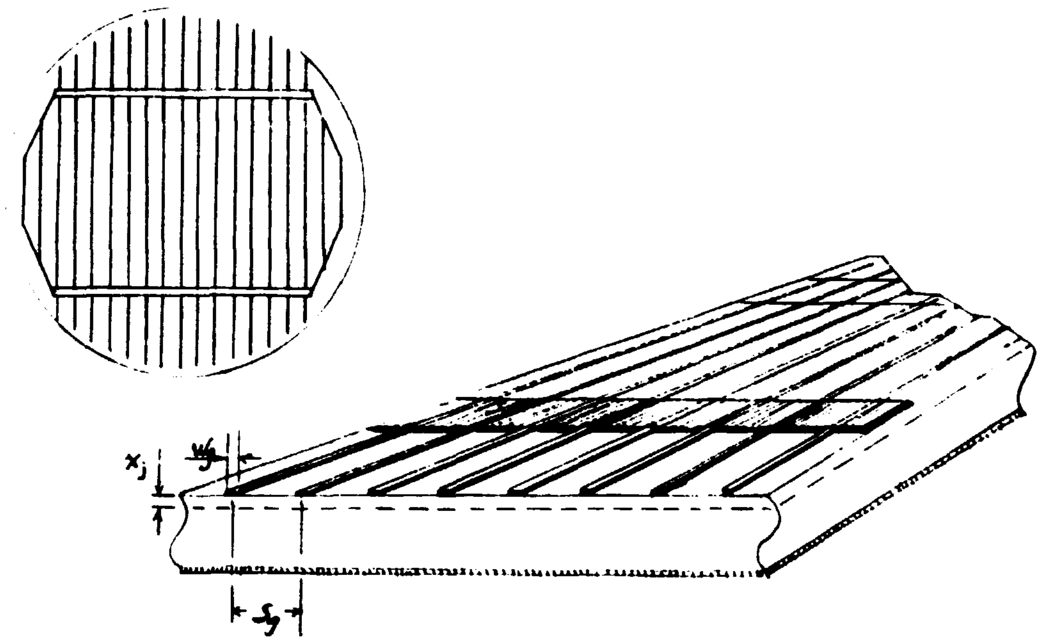


Figure 2. Typical Values

| APPLICATION | $X_J$ MICRON | $W_g$ MICRON | $S_g$ MM. | EFF. % |
|---|---|---|---|---|
| SPACE | 0.1 | <50 | 1 | 14 |
| TERRESTRIAL | 0.35 | >150 | 3 | 12 |

## Figure 3. Metallization Requirements

1. Low resistance ohmis contact
2. Avoid performance degredation
    - junction shunting
    - minority carrier lifetime
3. Good adhesion
4. Long term stability

## Figure 4. Evolution of Space-Cell Metallization

1. No illuminated surface metallization
2. Electroless nickel front surface grids
3. Evaporated titanium - silver, solder coated
4. Ti-Pd-Ag (passivated)

## Figure 5. Attributes of Plated Contacts

1. Small capital investment
2. Amenable to low cost, high volume batch process manufacturing
3. Additive process limiting material costs
4. Insensitive to surface irregularities

Figure 6. Ni-Si Alloy System

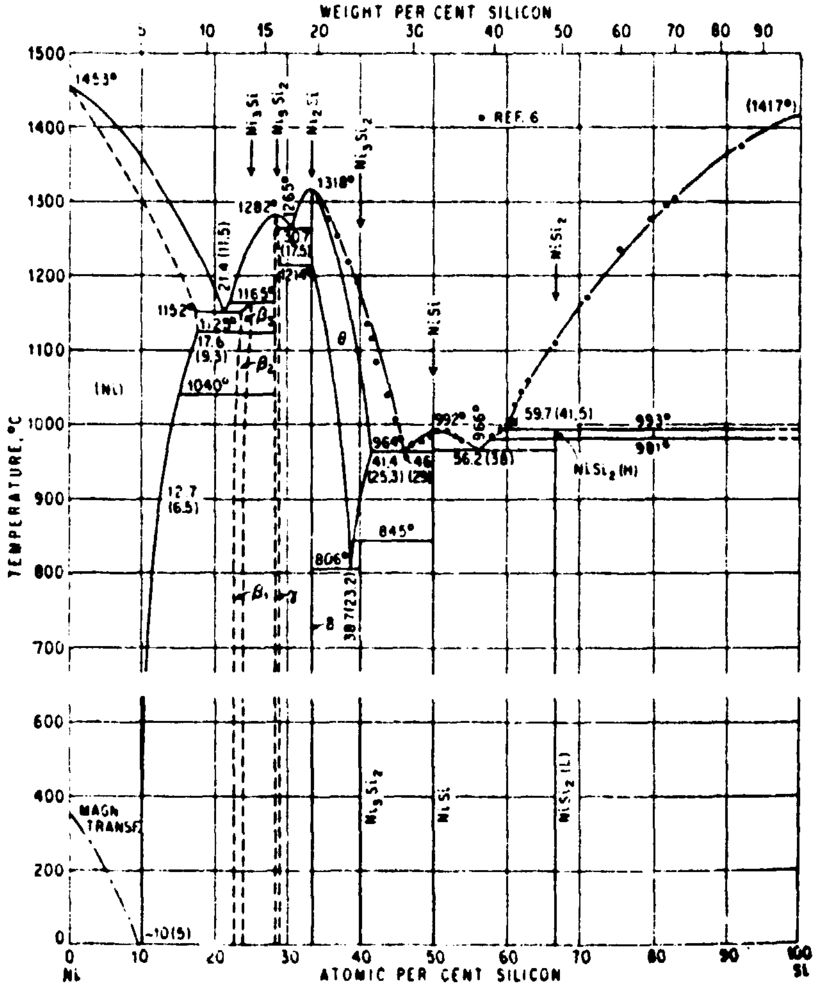


Figure 7. Effect of Sintering on Adhesion of Electroless Nickel Contacts

| Sinter Temperature* | Peel Strength |
|---|---|
| No Sinter | 90 grams |
| 200°C | 332 |
| 250 | 391 |
| 275 | 510 |
| 300 | 618 |

*20 seconds sintering time

Figure 8. Pd–Si Alloy System

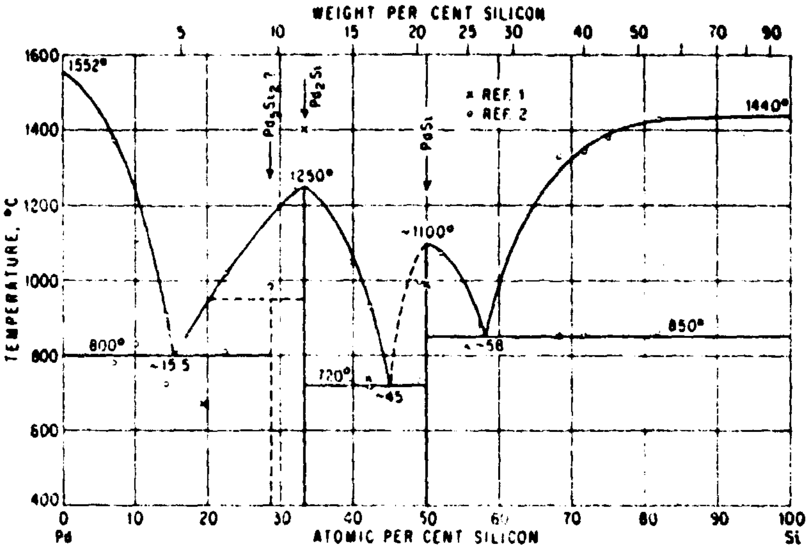


Figure 9. Au–Si Alloy System

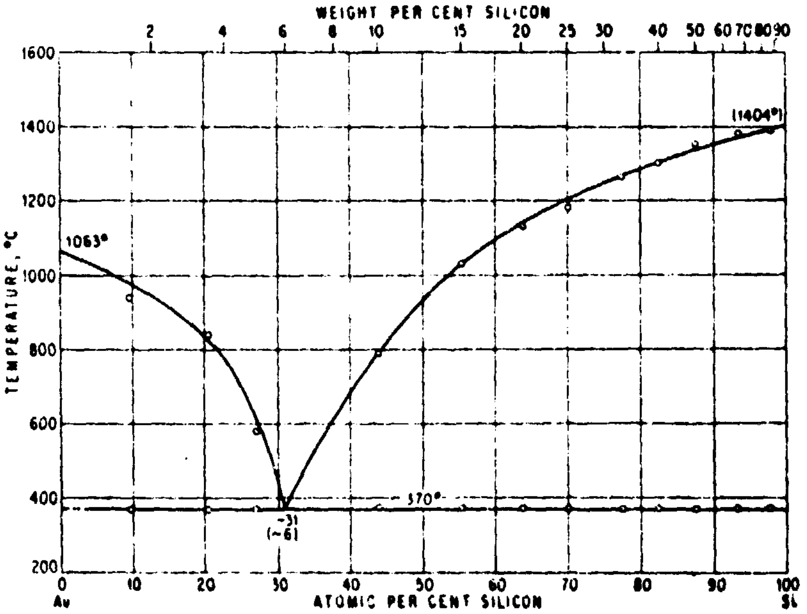
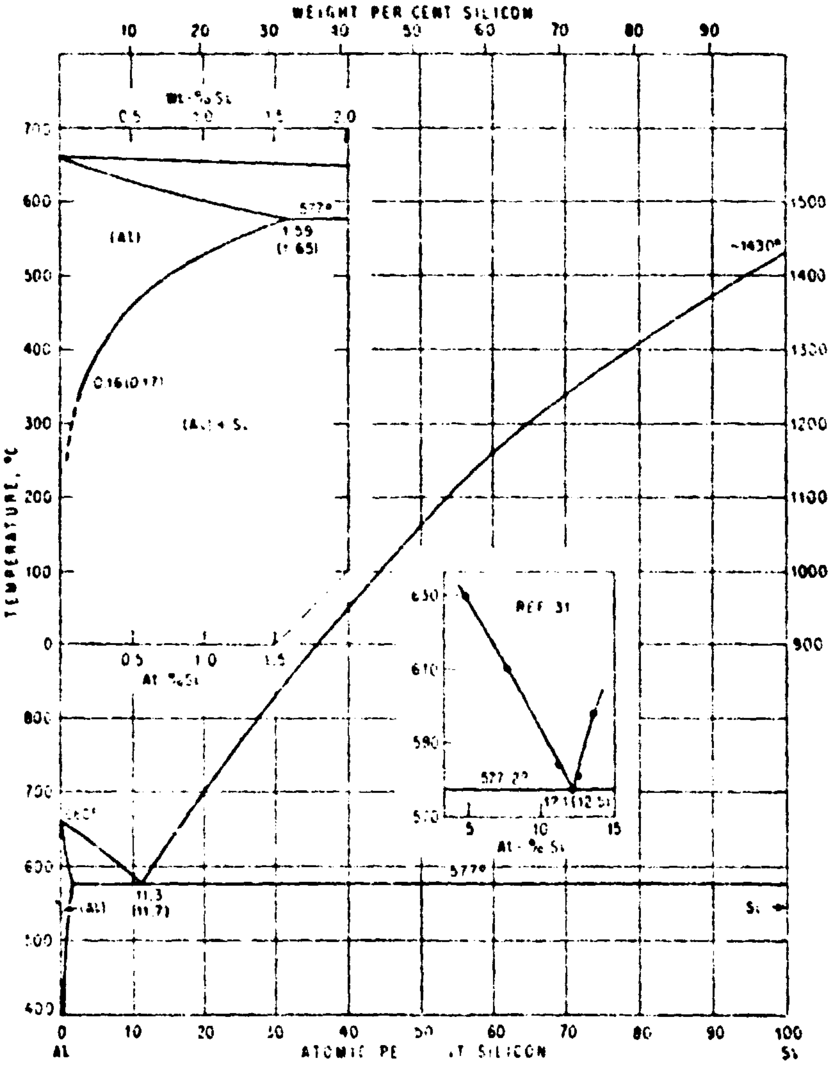


Figure 10. Evolution of Plated Contact Technology

1. SIMPLE ELECTROLESS NICKEL PLATING WITH SOLDER COAT
2. USE OF AR COATING AS PLATING RESIST
3. USE OF AU OR PD TO PROMOTE ADHESION AND OHMICITY
4. COPPER PLATING TO REPLACE SOLDER COAT

Figure 11. Aluminum-Silicon Alloy System



## DISCUSSION

WOLF: Thank you very much. At least we have advanced tremendously with our metallization problems at a time when most of the pottants were not well understood, particularly these questions of residual chemicals being interfaces -- interacting with environments -- which led in early times to customers concluding that you might as well ship the contacts in one box and the cells in another.

NICOLET: I would like to make a couple of comments. The first one has to do with the nickel-copper system. Nickel and copper form a solid solution, so I think it is evident that by combining these two elements you don't have a stable system. By stability I mean if you wait long enough it will change. The second comment is perhaps worthy of note here. We did investigate the matter, and we found to our surprise that the palladium-silicon phase diagram that you projected, from Hanson, is wrong. The nickel-and-platinum-based systems with silicon are also wrong. If you are interested I can give you a later reference. It surprised me these things are so old and yet not fully understood. PdSi is peritectically dissociating at 7°C.

TAYLOR: I agree with your first comment about the copper-nickel system. If you wait long enough or if you expose the system to high enough temperature, copper is going to migrate. Pryor and coworkers at Motorola have looked at that problem and have shown that for 20-year life, the copper-nickel system is a viable system. With respect to the phase diagram, I find this to be a very interesting question, I have looked at those phase diagrams and there is something about those diagrams that has to be wrong. I think that what we are seeing there is that the early phase-diagram work looked at reactions going on at fairly high temperatures and then they just dropped everything down to lower temperature. We are now dealing with systems in which we are using the low temperatures, and those same reactions are going on, and I think that a reevaluation of those types of systems is a thing we need.

WONG: Bill, I have a question. When you showed the gold silicon phase diagram I saw no significant solubility between those two constituents; I wonder whether you couldn't have adhesion problems at the gold and silicon interface, because thermodynamically it is hard to form the interface.

TAYLOR: Well, one certainly has a certain amount of solid solubility. The diagram I use there was taken from a fairly accurate reference. The solubility is so limited by the chart, there is no way one can get good adhesion.

LAVENDEL: I would like to complement your information on the use of welding to titanium-palladium-silver systems in this country. Lockheed has a very extensive program with respect to solar arrays where the welding of copper interconnect to silver metallization is used. At this present moment extensive tests equivalent to the low earth orbit for five years -- -80° to +80°C cycles -- have been performed and very little damage to the welds were found. We found some traces of some problems that might not be connected to fatigue but might be connected to entrapment of these pottants in some of the silver compound.

TAYLOR: Yes, I was aware of the Lockheed program and I think you people are perhaps farther along than anybody else that I know. This is still a program that is being proven out.

LAVENDEL: It could be applied to one of the coming shuttle flights.

TAYLOR: I don't think it has as yet been applied. There is in this country a program that was initiated by NASA to reopen the whole subject of welding technology. I have not heard what has been happening this past year. I am sure there is a lot of interest on the part of space people in welding technology.

STEIN: We have done a lot of work on ultrasonic aluminum wire and ribbon bonding to silver-bearing conductive coatings, such as the silver that might be used on a silicon solar cell. We haven't done this on silicon itself as a substrate. However, with some systems we see age stability and thermal cycling stability comparable, certainly, in an accelerated way, to 20 years of life. It is a bit different from welding.

TAYLOR: Thank you for your comment. I don't really have anything to add there. I know that is a technology that is being worked on.

WOLF: We will proceed to the second speaker of the session.