Silver Plating of Solar Wafers in Production.

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With the drive to find renewable energy sources the market for Solar Energy has increased substantially over recent years and is predicted to continue with this growth. Traditionally the wafers used, in this market, have been screen printed with a silver paste to form a silver conductor when fired.

Silver plating has been with us for many many decades. Changes to formulations required to service the electronics industry drove changes to formulations that had been around for some time.

There are limits to what can be achieved in terms of efficiency of conversion from Solar Heat to Electricity by this traditional screen printing. Therefore the potential to use silver plated conductors is being looked at seriously.

This paper/presentation will look at the links now between the two technologies, 1) Traditional Screen Printing of the Silver and 2) Silver Plating. How previously used technology from the silver plating of electronic components is now being used for this developing technology and how this is now moving to the production environment.

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Introduction

With the drive to find renewable energy sources the market for Solar Energy has increased substantially over recent years and is predicted to continue with this growth. Traditionally the wafers used, in this market, have been screen printed with a silver paste to form a silver conductor when fired.

Screen printing silver films for electronic applications has been with us for a number of years. In this method a paste, (containing) silver, is squeezed though a patterned mesh onto the silicon wafer. At this stage the wet film is around 25 microns. This screen printed silver paste, containing at least 70% silver, will form the conductor once it has been fired at 700 degrees C, through an anti-reflective coating, creating a bond to the silicon creating the circuit. The fired film will be around 12 microns in height. Generally the track width of the conductor will be around 100 microns and the wafer thickness itself around 160-200 microns.

Silver plating has been with us for many many decades. Changes to formulations required to service the electronics industry drove changes to formulations that had been around for some time. For the major part silver plating is used in high speed applications for the electronics industry now.

There are limits to what can be achieved in terms of efficiency of conversion from Solar Energy to Electricity by this traditional screen printing. Therefore the potential to use silver plating to improve the conductors is being looked at seriously.

This paper will look at how the two technologies are being merger together to give benefits for the plated coating whist managing the high outputs required for this industry.

History of Silver Plating

Silver plating baths have been around for some 100 + years. Originally these solutions were produced from alkaline cyanide electrolytes by dissolving silver cyanide in a solution of sodium cyanide. With the discovery that potassium salts, because of their purity, produced "cleaner" baths came the use of silver potassium cyanide (known as the double salt) in making up baths. This eliminated the use of "dusty" silver cyanide, simplified replenishment and overcame the need to filter residues. The general properties and hazards from traditional silver baths can be seen below. (See table 1, Silver Plating Chemistries).

Silver	Colour – white as deposited (traditionally the whitest). Density, 10.5g/cm^3.
	Matt – Semi bright for electronics and fully bright for decorative applications.
	HAZARD – CYANIDE, SEMI METALS (such as Antimony).

Conventional Silver Plating.

Because of the tendency for silver cyanide plating baths to produce poorly adherent immersion coatings the use of a strike bath has always been necessary. Silver strikes are usually operated at room temperature and have a low silver content with a high cyanide content in order to cause a strike of adherent silver onto the base material. Plating times are very short in order not to produce powdery deposits.

The mechanism of deposition is from the complex silver cyanide ion as shown in equation

$$Ag(CN)_2^- + e > Ag^{\circ} + 2CN^-$$

Traditionally these high cyanide (100 –150g/l KCN) silver baths used silver sheet anodes to form the complete replenishment circle. However dog bone shaped or corrugated shaped anodes were also very popular as are different types of silver grain (traditional, exploded, popcorn etc) used in baskets are now.

Originally silver was almost totally used for decorative applications. The rapid increase in the price of gold during the sixties/seventies saw the use of silver increase substantially, in the electronics market where its tendency to migrate, tarnish or give reduced electrical properties gave no performance problems.

When coupled with semi-metallic (decorative) or organic (decorative and electronic) brighteners silver cyanide based plating baths became very popular, due to their ease of operation, consistent satisfactory deposits and ease of effluent treatment, for both the decorative and electronics market …..and this is still the case today.

However, these simple silver baths developed further for the electronics industry during the seventies due to the need to produce very high speed plating silver solutions, in order to meet the needs of the electronics industry for semi conductor components on PCBs. The requirements from the semi-conductor market for selectively silver plated lead frames saw a new generation of silver processes developed. These processes were originally claimed to be non-cyanide systems but were actually low cyanide systems. True, on make up there would be no free cyanide found but due to replenishment by salt only they did build up some free cyanide during their life.

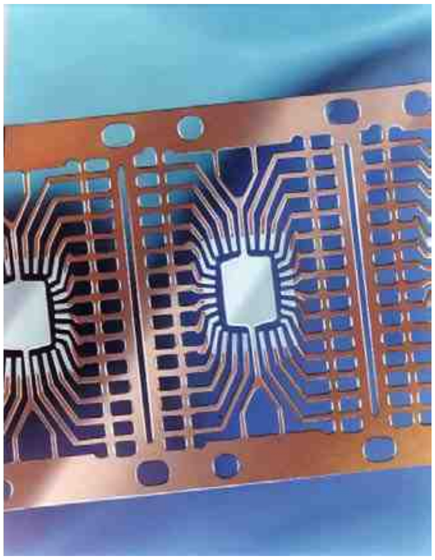
Electronic Innovation.

Low Cyanide High Speed Silver Plating (See table 2 & 3, Low Cyanide Silver Chemistries).

As the electronic industry emerged fully during the seventies the need to plate silver at high speeds became very apparent. High Cyanide bright silvers were being used in a large numbers for barrel plating parts extremely successfully. However these baths showed limitations when being used at high current densities on high speed reel to reel lines and selective spot lines in particular. The requirement to selectively plate silver spots onto lead frames required vastly different plating conditions and parameters, therefore a new range of silver plating solutions were developed to meet these new demands. The silver plating processes developed although still using the “double” salt silver potassium cyanide were very different from conventional silver cyanide baths.

These low Cyanide Silver plating processes have now been with us since the early seventies. Due to the fact they do not contain any free cyanide there is no capability to dissolve silver anodes. They therefore use DSA (dimensionally stable anodes) such as platinised titanium. They contain **zero free cyanide** on make up and are silver replenished by the addition Silver Potassium Cyanide. Generally the baths have a finite life due to density build up and traditionally will have around 20g/l Free Cyanide at the end of there life. The conductivity of the process is supported by either phosphate or nitrate chemistry to replace the cyanide. They usually contain some ppms of semi metal (and sometimes a wetting agent) to grain refine the deposit.

Example of a selectively silver plated lead frame used in the electronics industry. Plated on a high speed selective silver plating line at high current density.



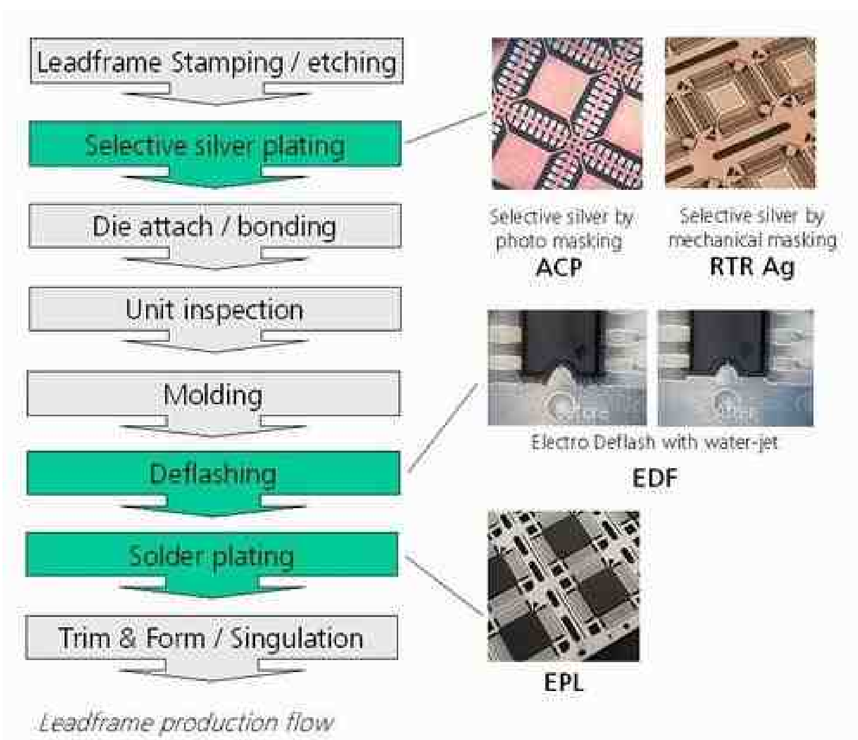
FEATURES AND BENIFITS

Low Cyanide	:	Safer Working Environment
Low Cyanide	:	Reduced Heath and Safety Costs
Low Cyanide	:	No need for Silver Strike in Pre-treatment
Low Cyanide	:	Reduced Environmental Impact
No other Pollutants	:	Reduced Environmental Costs
Extremely Fast Plating Rates	:	High Production Levels

Operating Parameters of Low Cyanide High Speed Silver Plating

Usual Working values			**Permissible Working Range**		
Content of Silver		65 g/l	Content of Silver		50.0 to 80g/l
pH-value		8.5.	pH-value		8.0 to 10.0
Working temperature		65°C	Working temperature		40 to 70°C
Cathode current density			Cathode current density		
	Phosphate	20 A/dm^2		Phosphate	up to 80 A/dm^2
	Nitrate	100 A/dm^2		Nitrate	up to 250 A/dm^2
Cathode current density			Cathode current density		
	Phosphate	200 A/ft^2		Phosphate	up to 800 A/ft^2
	Nitrate	1000A/ft^2		Nitrate	up to 2500 A/ft^2
Deposition rate			Deposition rate		
	Phosphate	1.0 µm/10 seconds	Current Density		10 A/dm^2
	Nitrate	1.0 µm/2 seconds	Current Density		50 A/dm^2

Examples of silver plating (and process sequence) on lead frame.
Courtesy of Meco Equipment. (www.meco.nl)

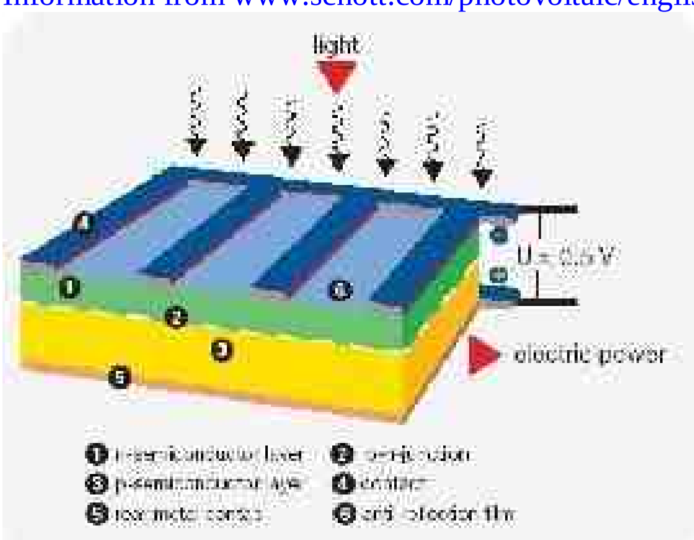


Use of Silver Plating processes for Photovoltaic markets.

As we know there has been a great deal of discussion over the last decade regarding the objective of clean renewable energy sources to replace carbon based products. One such technology is to use silver as a conductor to transform solar energy into electricity via a silicon wafer. Over the recent years this market to manufacture these products has grown substantially.

Traditionally the silver conductor is applied by screen printing a silver paste onto the silicon wafer which has an anti reflective coating applied. On firing the silver paste will burn through the anti-reflective coating creating a bond to the silicon creating the circuit.

Information from www.schott.com/photovoltaic/english.



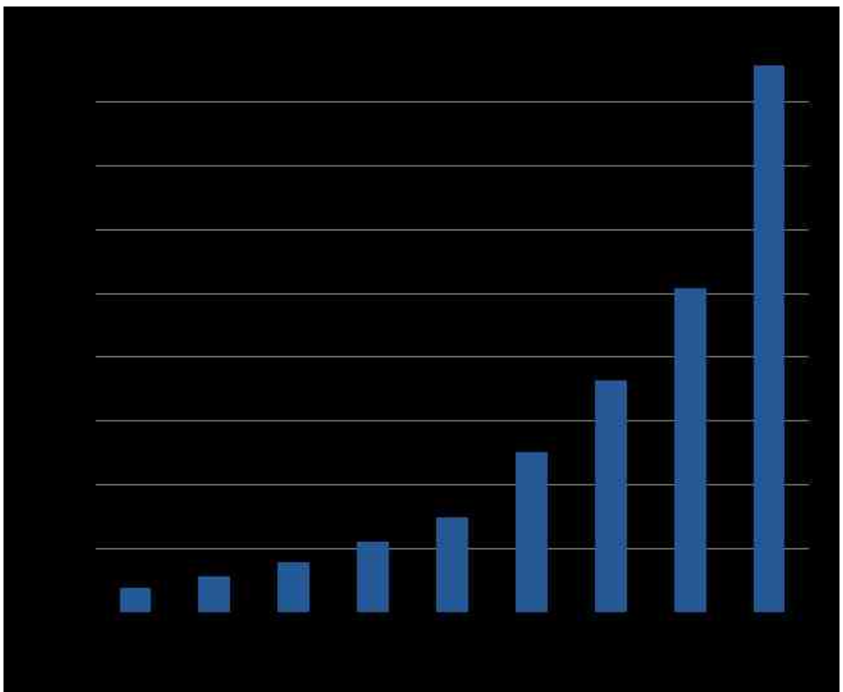
Information regarding the technology to convert the sunlight to electricity can be found on many websites.

Market Information

This market has and is growing substantially and is a significant user of silver metal as paste. The following market information clearly shows why it is now such an interest for plating.

World solar photovoltaic (PV) market installations reached a record high of 1,744 megawatts (MW) in 2006, representing growth of 19% over the previous year. This was completely overshadowed by the 2007 figures with a 38% growth rate.

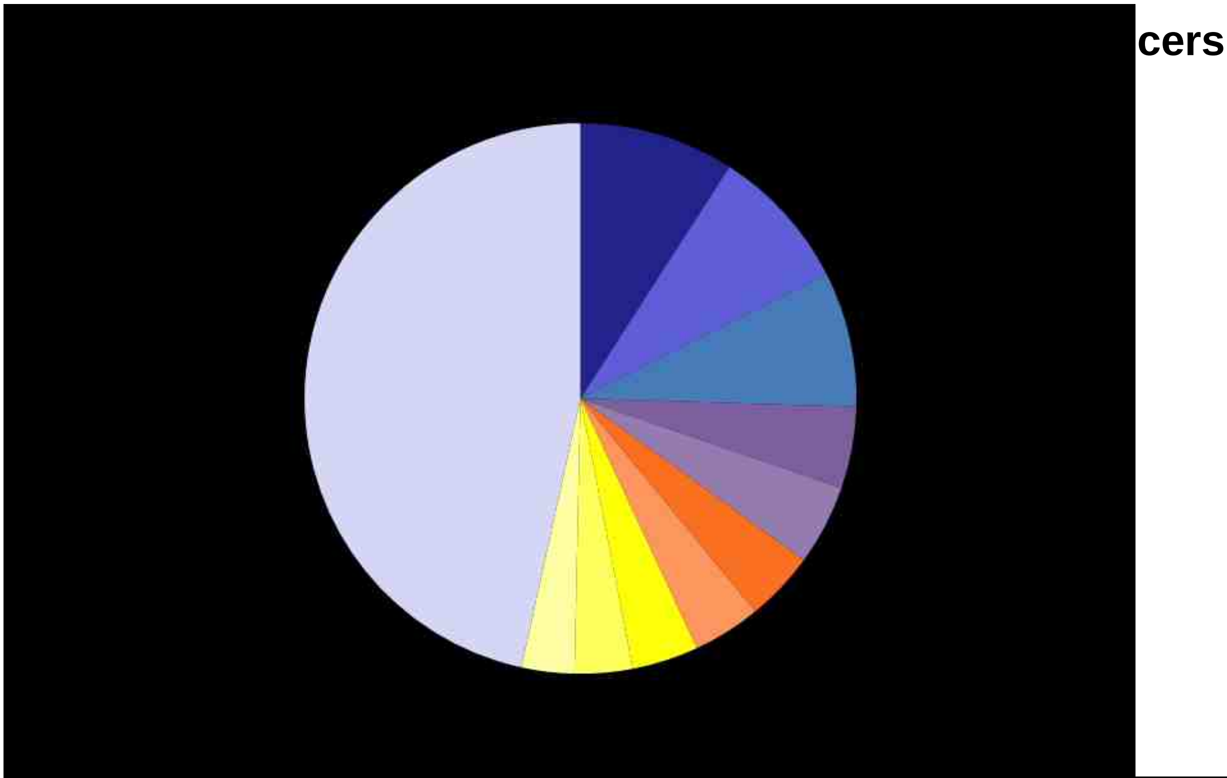
Photovoltaic Production (MW_p)

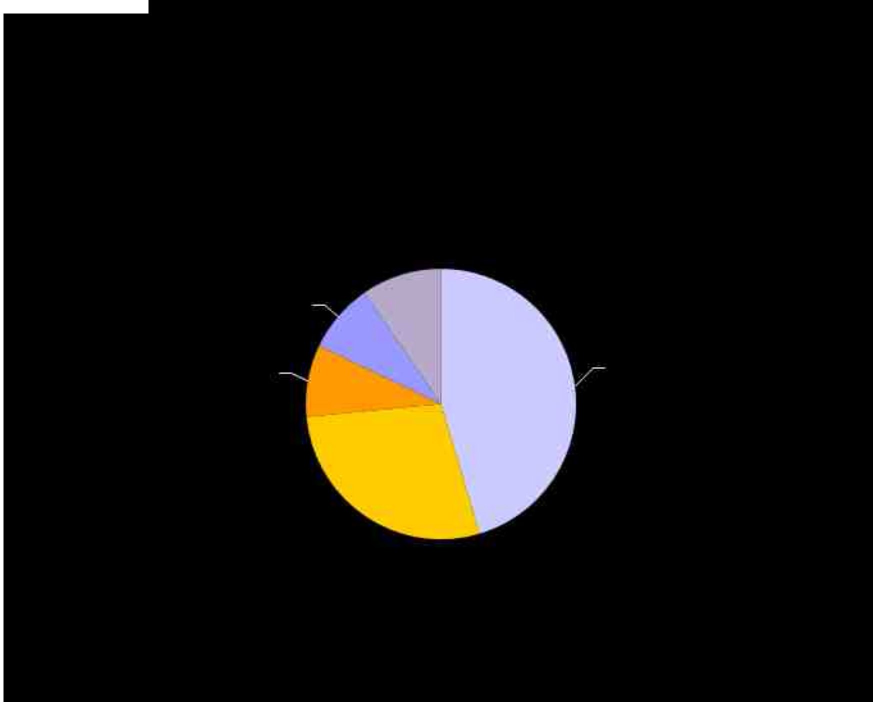


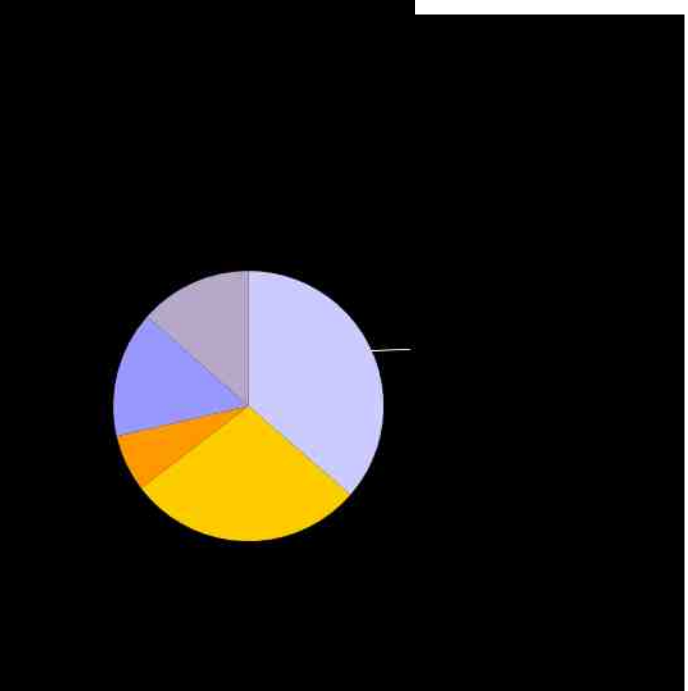
2006 global solar paste market > 350 metric T
Equivalent to 245 metric tonnes of silver

Photon International 2008

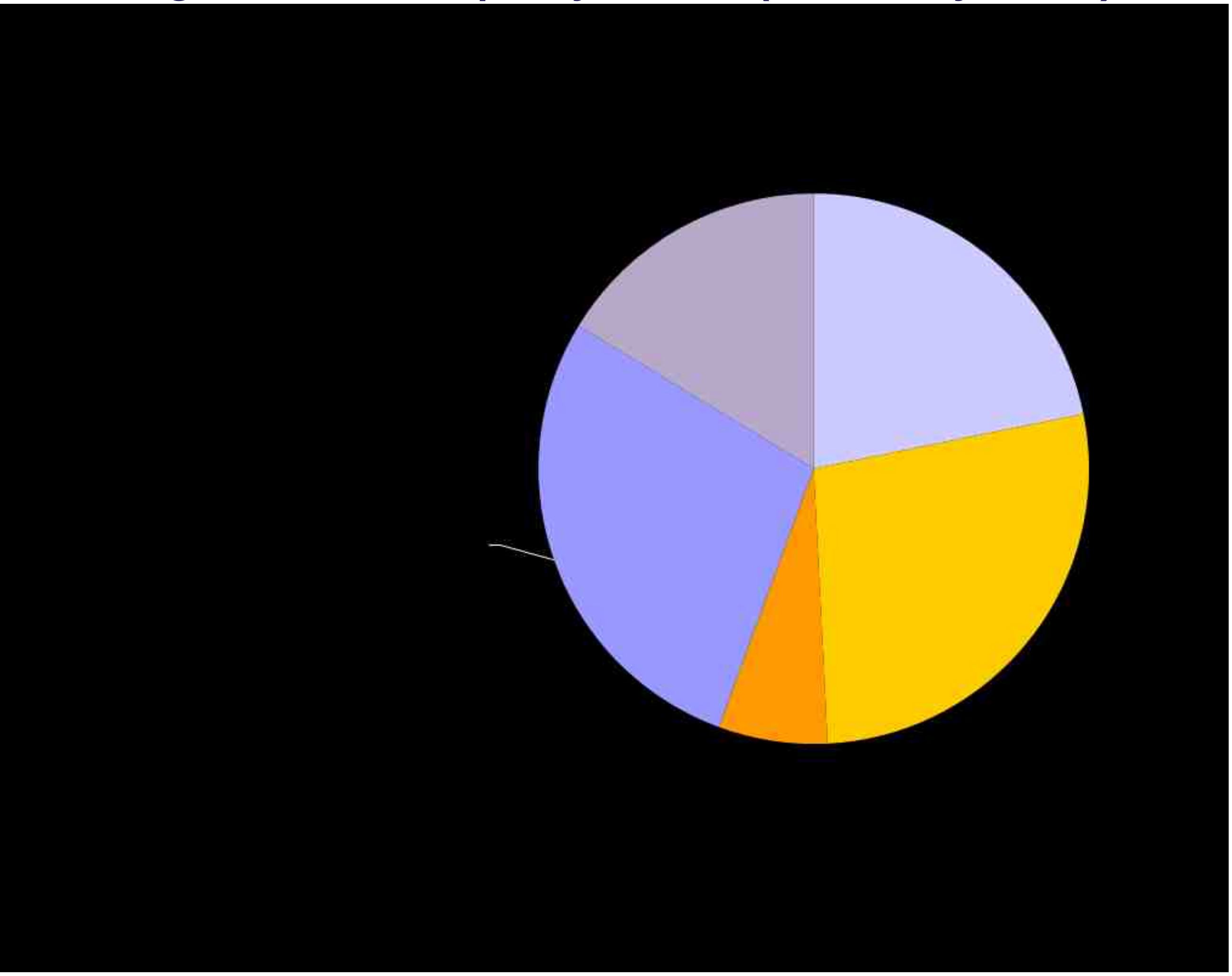
If we look at the main producers it can be seen that roughly 1/3rd of the producers are each in Europe, Japan and the rest of the world.



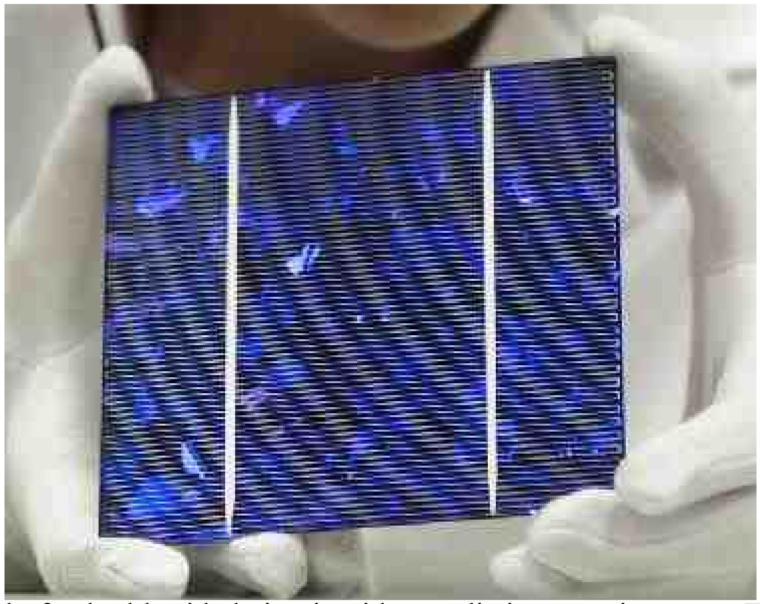




Significant overcapacity in RoW (essentially China)



The Solar Panel



The solar cell is comprised of a double sided circuit with two distinct requirements. The"front side" comprises of an antireflective coating (silicon nitride is commonly used) and the silver conductor. Traditionally this silver coating is screen printed.

Silver Front Side Metallisation

Requirement:

Efficient contact through anti-reflective coating
High line conductivity, i.e. low Series Resistance (Rs)
Good line resolution and high Aspect Ratio
Good solderability
Pass mechanical tests /thermal ageing

The second half of the circuit is the aluminium backside metallisation. Here the Aluminium is used to contact the back side and to generate a « Back surface Field effect » (BSF)

Aluminium Back Side Metallisation

Requirement:
Good ohmic contact
Good BSF formation
Low Bow

Paste composition for the silver "front side" paste.

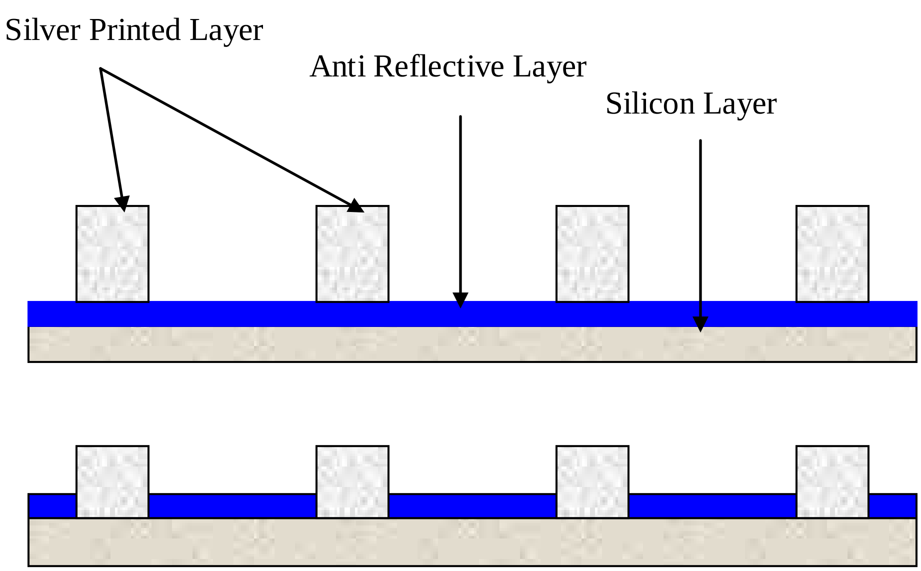
Conductive fine powders and/or flakes
Glass frit to promote contact and adhesion
Organic medium to provide good printing characteristics
Additives for boosting, bonding…

There are also cells parameters affecting metallisation performance

Si Orientation (mono, multi-crystalline)
Structure of the ARC - SiNx, TiOx (chemistry , texture, thickness, density…)
Sheet resistance emitters (P dopant, deepth, carrier…)
Firing profile (temperature, side up)

Schematic of the process

a) Traditional (Schematic license – Actual screen printed layer is curved)



In this traditional method the screen printed silver layer fires through the anti reflective layer and becomes the total silver conductor layer

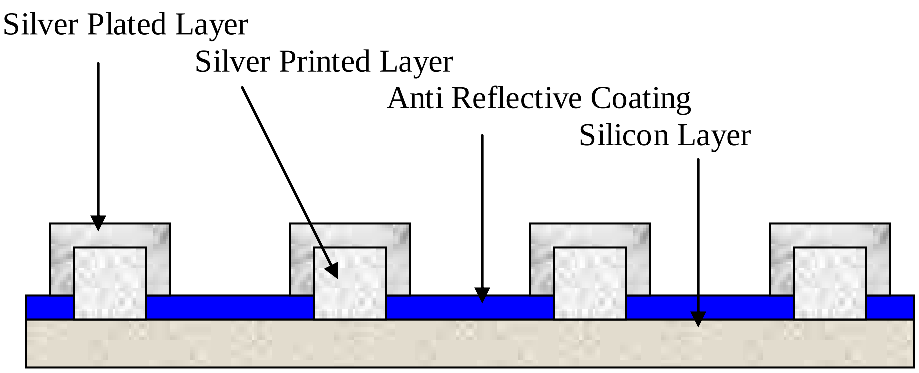
New process opportunity.

The requirement for the silver conductor is to have as continuous, consistent, conductive silver layer as possible. Due to the technique of screen printing the fired films is not as continuous as needed.

There are therefore now moves to apply a plated coating. The technique is to fire a thinner coating of a narrow track width silver screen printed coating which is then used as the seed layer. The silver plating then can be applied very easily to this screen printed coating, plating 10 microns of a continuous pure silver layer. Efficiency increases in the transfer of solar energy collected to electricity makes this application of this technology very interesting to design engineers.

Issues such as 1) handling of the thin wafers, in order to achieve realistic plating production times and 2) the new inks required in order to, achieve a fine dense, thin, narrow layer are both areas being overcome. A new process technology involving silver electroplating is now available.

b) New method (Schematic license – Actual screen printed layer is curved as is plated layer)



In this new method the thinner, narrow, screen printed silver layer fires through the anti reflective layer and is then over plated with 10 microns of silver. This total combination then becomes the total silver conductor layer

Plating can be achieved with some ease as the screened material is very susceptible to plating. However in order to achieve realistic production quantities the high speed silver plating solutions, detailed above, need to be utilised together with high speed plating plants.

Details of this high speed plant and the results obtained, with the above high speed solutions, are seen below.

THE PLANT.

Meco Pilot Line
Cell 0.6 metre
Capability 200 wafers hour

In this new system, the wafer is held in a stainless belt where contact is made to the one side to be plated. The wafers are transported , held by this belt, along the line through the plating cell or plating cells. The line can be multiples of cells depending on the production quantities and hence lines peed/current density. The solution is held in a sump below the cell and is pumped up to the cell where a weir system controls the depth of the solution. The process sequence is very straightforward.

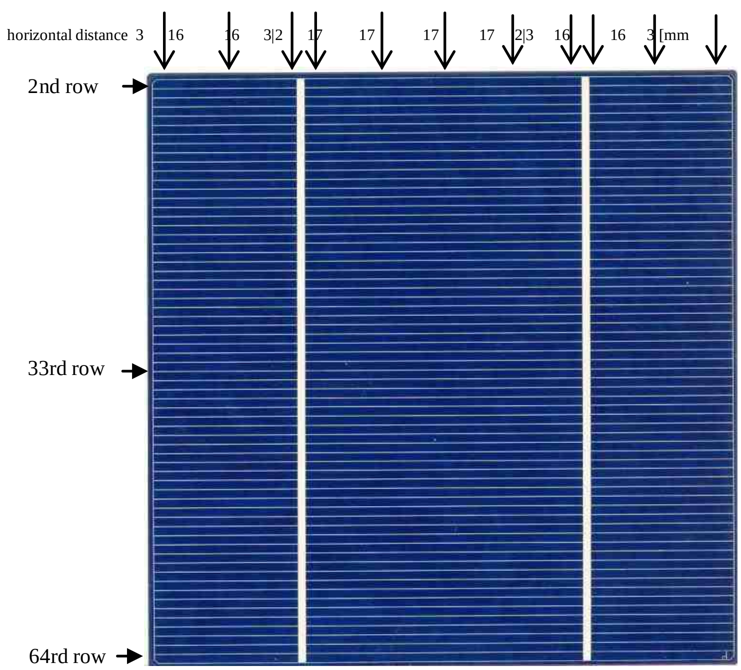
Process Sequence.

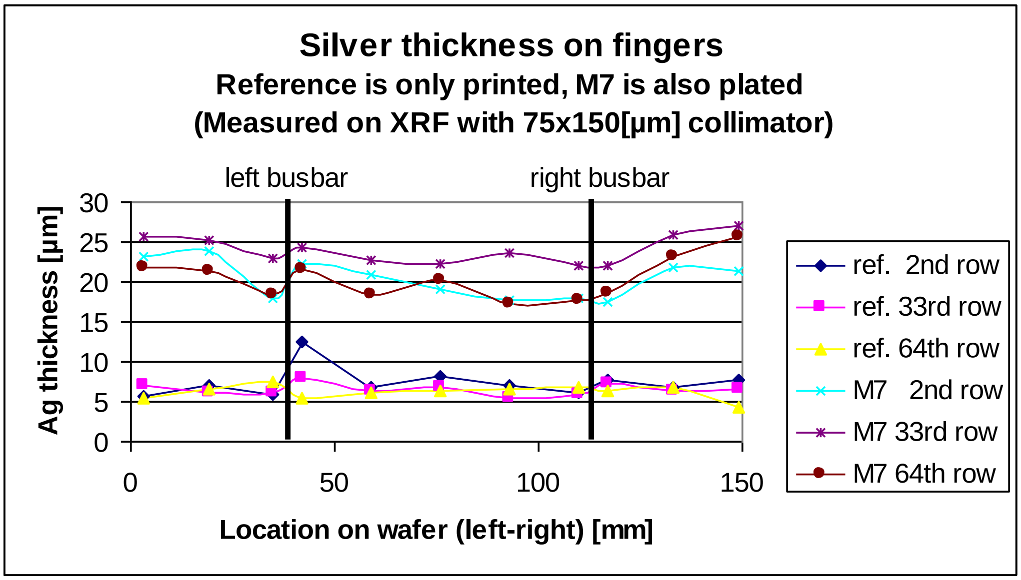
Load
Conditioning
DI Rinse
Ag Plate
Drag Out Rinse
DI Rinse
Blow Off and dry
Unload

On the reverse side of the plant any small amount of silver plated onto the belt is stripped rinsed and dried. The belt then continues to the load station.

Results

Wafers were plated in this cell at between 5A/dm^2 and 25A/dm^2. The wafers were already printed to full thickness so the evaluation was to see what speed of deposition could be achieved and the distribution that would be achieved. A number of measurement points along the wafer was identified for measurement and the graph below details one set of results.





It can be seen that the distribution was extremely good from this set up and that extremely fast current densities of 25A/dm^2 could be achieved. This gave plating times in the cell of down to 30 seconds.

Environmental issues

Silver plating has been with us for some time and will continue to be a useful deposited metal. Respect for toxic materials within the industry has minimised accidents and injuries and silver cyanide plating has its part to play for some time still. Improvements in effluent treatment and treatment of air emissions have reduced the environmental impact. Clearly the need for non cyanide systems will develop as these environmental pressures persist.

Conclusions & Summary

The silver plating of the solar panels is quite straightforward. A pilot manufacturing/plating lines has been establised and many wafers plated. The silver distribution on the plated wafers is very promising, especially when you keep in mind that only single wafers were plated and no attampts were made for any kind of shielding! The silver thickness increase on the fingers (15[µm]) is higher than on the busbars (7 [µm]). The theoretical thickness (12 [µm]) is between these two values. The actual amount of silver to be plated onto the fingers can be optimised by chemistry, line speed, shielding etc.

New opportunities are therefore offering themselves in the photovoltaic market for silver plating. Handling issues both in terms of production output and environmental concerns are being overcome. Silver plating will therefore play a part in this exciting emerging technology.

Table 1 Silver Chemistries. (SPC = Silver Potassium Cyanide)

Silver	SPC	SPC	SPC	SPC	SPC	MSA + Ag
Application	Industrial Decorative	Decorative	Industrial	Industrial	Industrial	Industrial
Type	Rack	Rack	Rack	High Speed	High Speed	Rack
	Barrel	Barrel	Mid HS			Barrel
Silver	36g/l	36g/l	50g/l	65g/l	65g/l	30g/l
Cyanide	150g/l	150g/l	70g/l	0-20*g/l	0*-20g/l	0g/l
Complexant	-	-	-	-	-	120g/l
Additive	-	-	-	-	0-5ml/l	-
Brightener	Organic	Antimony	Selenium	Selenium	Selenium	Organic
Temperature	25ºC	25ºC	40-60ºC	40-60ºC	40-60ºC	20ºC
Current Density	1.2A/dm^2	1-2A/dm^2	1-7.5A/dm^2	10-50A/dm^2	50-200/dm^2	1.1A/dm^2
Plating Rate	1 micron 1 minutes	1 micron 1 minutes	1 micron 10 seconds	1 micron 4 seconds	1 micron 2 seconds	1 micron 1 minutes
Agitation	Moderate	Moderate	Vigorous	Vigorous	Vigorous	Moderate
Hazard	Toxic	Toxic	Toxic	Toxic	Toxic	None

*** Made up at 0g/l free cyanide but builds up to 20g/l during bath.**

Table 2 Low Cyanide (Phosphate Type) Silver Chemistries.

PARAMETER	**UNIT**	**RANGE**	**OPTIMUM**
Silver	G/l	55 - 75	65
Conducting Salts	G/l	110 - 150	130
Brightener	Cm^3/l	0 - 3	2
Wetting Agent	Cm^3/l	0 - 3	2
PH		8.0 - 9.0	8.5
Solution Density	^{o}Bé g/cm^3	14 - 22 1.107 - 1.180	18 1.143
Temperature	^{o}C	45 to 60	
Current Density	ASF A/dm^{-2}	up to 800 up to 80	

Table 3 Low Cyanide (Nitrate Type) Silver Chemistries.

DESCRIPTION	UNIT	RANGE	OPTIMUM
Silver Concentration	g/l	50 - 80	65
pH (electrometric)		8.0 - 10.0	8.5
Temperature	°C	60 - 70	65
Current Density	A/dm² A/ft²	45 - 220 500 - 2500	as required as required
Specific Gravity	 °Bé	1.12 - 1.16 16 - 20	1.14 18
Cathode Efficiency	%	85 - 95	-

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