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REVIEW ON FRONT CONTACT METALLIZATION PASTE USING SILVER NANO PARTICLES FOR PERFORMANCE IMPROVEMENT IN POLYCRYSTALLINE SILICON SOLAR CELL

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Abstract - ***This paper presents the exploitation of nano technology in the preparation of silver metal paste of front side metallization of polycrystalline solar cell for improvement in performance and efficiency of solar cell. Photovoltaic (PV) is the technology to convert sunlight directly into electricity. Metallization for the solar cell is the technique through which the extraction of photo generated current from the solar cell takes place, when the sunlight strikes the surface of the solar cell. This technique is applicable to both types solar cells i.e. single and polycrystalline. Typically, the structure of a crystalline solar cell fabricated on silicon wafer is mainly a p-n junction. Metal contacts to both the n and p type sides of the junction are used to collect electricity for commercial crystalline silicon solar cells. Metal contacts are usually formed by screen-printing a silver paste which is then densified by a firing treatment process at high temperature. Usual conventional silver paste used for front side metallization have a significant shrinkage of silver paste during firing treatment and it is difficult to achieve silver electrodes with high aspect ratio, this causes high shading losses caused by a large percentage of front side metal coverage. By using advanced nanotechnology the overall performance can be improved. By using nano particles of silver metal (in nano range of 1-100nm) the shading losses reduced, aspect ratio increased, conductivity increased and efficiency of solar cell will be increased, cost of solar cell with reduction in silver metal also reduced.***

Key Words: *Polycrystalline solar cells, Metallization, Printing, Drying, Firing, Silver nano particles and Solar cell efficiency etc…*

1. Introduction

Research work concentrated on metallization to increase of efficiency and reduction of total cost of solar cells.

The current interaction in solar cells is based on the compatibility of the metal paste with base structure of the semiconductor materials. The properties of the metal pastes like viscosity, density, electrical conductivity, adhesion properties, organic compounds and curing of the solar cell with respect to the time is important.

Thick film and thin film technologies are available for metallization [1] [2].

Commercial screen printable silver pastes used for front side metallization to form a metal grid which extract photo generated current from a solar cell. The resistivity of the metal paste is very important from power loss point of view. The advances made in paste formulation by using nanotechnology to increase conductivity, high aspect ratio and overall increase of efficiency of solar cell by reducing power loss. By using nano particles of silver metal and glass frit conductivity increase, power loss decreased. This is due to novel unique properties of high surface to volume ratio of nano particles, excellent thermal, electrical, optical and catalyzing properties due to their nano size effects.

2. Metallization for solar cells

In metallization the metal paste of a suitable metal which is chemically compactable with the base material of a solar cell is laid on the surface of the solar cell through screen printing technique. For this printing a suitable mesh is provided through which this paste is poured with significant pressure and corresponding structure of metal paste is observed on the surface of the solar cell; further the solar cell dried and then fired in a suitable furnace for the adhesion of the metal paste with the base metal of the solar cell [3].

3. Properties Required for Metal Paste

- Metal pastes are thixotropic in nature
- Viscosity in the range of 150-200Pa.s (The viscosity should not change during the application process and should be within ±25 to 50Pa.s).
- Shelf life (minimum 6 months or more).
- Levelling time.
- Drying time.
- Firing temperature in the range of 250ºC to 900ºC.
- Bonding mechanism should be frit less or mixed.
- Density.
- Electrical conductivity.
- Adhesion properties.

4. Metal paste Manufacturing Technology

The main technology which is used for the production of metallization pastes is the conductive filler dispersion technique.

Conductive filler dispersion process

a) Wetting

This process substitutes the air and moisture on a filler surface with vehicle. In other words, the air and the moisture on the filler surface are replaced with resin solution as they are deleted and the interface between solid and gas (filler/air) transforms into an interface between solid and liquid (filler/resin solution). The resin solution penetrates into the space between fillers. Such wetting depends on the shape of the filler particle, polarity of surface and amount of air absorbed in pigments. Hence, the wetting process is extremely important.

b) Grinding

This process grinds filler agglomerates into a proper size. In other words, filler agglomerates are grinded by mechanical force (primarily shock and shear) and particles sizes are reduced. Widely used dispersing equipments includes ball-mill, sand-mill, beads-mill and 3-roll mill. Dispersing equipments are selected accordingly to the viscosity of the paste and strength of the dispersion. Once the filler particle size is reduced by grinding, specific surface areas expand to increase the surface free energy and make the dispersion unstable. This results in re-coagulation of fillers that it is necessary to reduce the surface energy of pigment in order to prevent the re-coagulation.

c) Stabilization of dispersion

This process targets to prevent the re-coagulation of dispersed particles and precipitations [4].

5. Front Paste Composition

Metal pastes mainly includes Ag/Al main ingredients (70-80%), glass frits (5%) and solvents (3-15%).

Metallic contacts are based on the use of silver as a conductive metal and should have good contact properties with n type silicon and excellent solder ability (needed for the later interconnection of cells). To make the deposition of this metallic contact with a screen printing technique, with the goal of reaching a final correct mechanical adhesion to the surfaces and good electrical properties, special metallic pastes have been developed for the solar cell industry. Silver powder represents the 70-85% in weight of the commercial pastes with a mixture of different shaped particles, of different sizes (as spherical powder grains or flakes), that are responsible for the paste conductivity and final cohesion of the contact.

Glass frits are metal oxides that play the most important role in the formation of the contact because its function is to melt the dielectric layers (by forming eutectic alloys of lower melting point), that are deposited or grown on the silicon emitter, allowing the metal particles to reach the silicon surface. Additionally its contact determines the adhesion of the paste to the silicon substrate.

Organic compounds are used as a vehicle to transport the suspended silver and glass particles, allowing its disposal with the screen painting techniques. Among these organic compounds are : organic solvent to allow the mixture to be used as paint and organic binders to maintain the particles joined once the solvents have been evaporated (cellulosic resins) after transferring of pattern.

Other additives to modify the rheological properties of the mixture and its interaction with the substrate surfaces (wetting agents).

Apart from this the exact formulation of the metallization paste are kept as a industrial secret, but it is possible to summarize the general components of a typical front contact paste can be shown as follows.

Components	**Wt.%**
Silver	70-85
Glass Frits	0-5
Cellulosic Resin	3-15
Solvent (Pine Oil or Glycol Ethers)	3-15
Additives (Rheological Modifiers and Surfactants)	0-2

Table-1: Components of industrial screen printing pastes for the definition of the front contact.

Fig. outlines the characteristics of the pastes during the firing process. The steps in firing of metal paste when laid on silicon cell are as under [4],

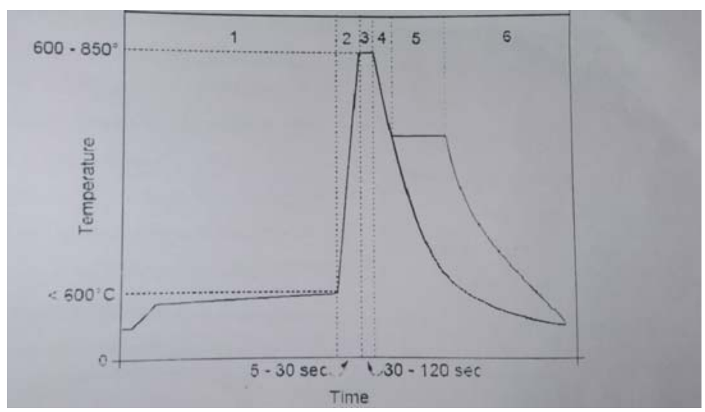

Fig-1: Co-firing temperature-time profile of solar paste firing process

1) Burn-out
2) Ramp-up
3) Peak
4) Ramp-down
5) Tempering step
6) Cooling.

6. Advances in Metal Pastes

Due to high and sometimes volatile cost of silver metal, the need for solar cell metallization pastes with lower silver content has become imperative.

Extensive research has been done on the development of front side pastes with decreased silver loading and

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deposit. Experimental results have indicated that a threshold exists for silver reduction, below this silver loading, the performance of the paste begins to significantly degrade. It was found that an increase in busbar-to-busbar grid line resistance with decreasing silver content was the primary source of degradation. By tailoring the solid content and morphology, as well as using proprietary additives, the performance of a low silver paste could be improved to the of the paste with a much higher silver loading. Thus research and development continuous to improve the performance-to-cost ratio of its PV metallization pastes to meet market demands and customer requirements.
Metal pastes are one of the key components that affect solar cell efficiency; especially front electrodes are known to have the greatest influence on the solar cell efficiency.

7. Paste Formulation Using Nano Particles

The silver paste for crystalline solar cells are prepared by the rotary evaporation method, specifically silver particles 80 wt % micron particles and nano particles in ratio (70:10), glass frit powders (4wt%) and organic vehicle(ethyl celluloses ad terpineol) (16 wt%) are mixed at a certain ratio (80:4:16) in ethyl alcohol. The contents are concentrated in a rotary evaporator at about 40ºC. After few hours, the ethyl alcohol can be eliminated and preliminary products are finalized by a three-roller-mill grinder.

The three-roller-mill grinder has widely been used in paste materials. The mill roller is usually made of high hardness alloy, which is also equipped with a cooling device for continuous operation. The final product (paste) thus obtained is ready for application on crystalline silicon wafers by using a screen printing machine followed by firing process in a conveyer infrared furnace.

Composition of silver paste contains mainly synthesised silver nano particles and micro particles in the range (50nm to 2µm), glass frit and organic binder. Lead free glass frit nano sized particles and silver nano particles are used to achieve high performance of crystalline solar cells.

Composition	Wt%
Silver particles (micro particles + nano particles)	(70:10) 80%
Glass frit (lead free)	4%
Organic vehicle (Ethyl celluloses + terpineol)	16%

Table-2: Composition of silver paste

Silver electrode formed by new prepared paste containing nano particles and PV performance measured.
For comparison, a reference silver paste (denoted as paste B) based on single micron silver particles was also prepared with the same composition ratio of the paste ‘A’ (80/4/16).

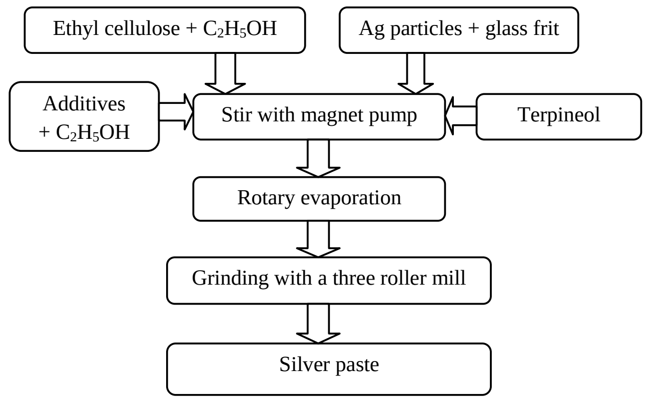

Fig-2: Flow sheet for preparing silver front contact paste

Silver fingers from paste B were also formed by screen printing on silicon wafers. Schematic diagrams of the two kinds of silver fingers before firing process were presented as shown in figure. Compositions of silver contact paste with silver nano particles (paste A) and without nano particles (paste B) was shown in table.

Past e ID	Silver particles	Glass Frit	Organic vehicle	Ratio
A	Nano particle aided	Bi-based	Ethyl celluloses + terpineol	70/10/4 /16
B	Micron	Bi-based	Ethyl celluloses + terpineol	80/4/16

Table-3: Composition of silver paste A & B.

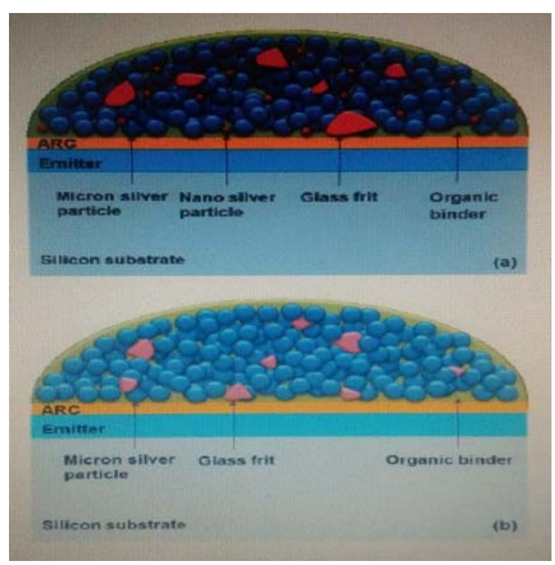

Fig-3: Schematic diagrams of the printed silver fingers before firing treatment: (a) Containing hybrid of micron

silver particles and nano silver particles, (b) Containing single micron silver particles.
It can be seen that the silver thick film fabricated from silver paste containing silver nano particles exhibits denser structure (fig. 3 a) than that of thick film based on silver paste containing single micron silver particles (fig. 3 b). The experimental results demonstrated that the silver nano particles which were added as a sintering aid into the silver paste, promoted sintering of silver particles.

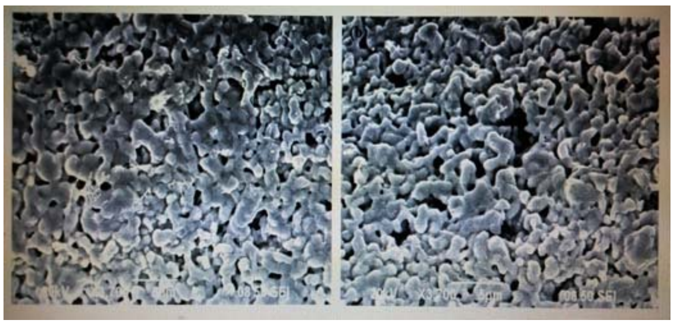

Fig-4: SEM morphologies of the surfaces of the silver thick film: (a) fabricated using hybrid silver particles and silver nano particles; (b) fabricated using single micron silver particles.

The photovoltaic performance of the fabricated crystalline silicon cells resulting from the silver pastes A and paste B were shown in figure 4. it can be seen that the fabricated silicon solar cell based on paste A containing silver nano particles generated an open circuit voltage (V_{oc}) of 622 mV, a short circuit current density (J_{sc}) of 34.6 mA/cm^2, a fill factor (FF) of 74.8% and a conversion efficiency (E_{ff}) of 16.1%. These are improved results compared with those resulting from the solar cell based on the silver paste B containing single micron silver particles (V_{oc} = 618mV, J_{sc} = 34.3mA/ cm^2, FF = 72.5%, E_{ff} = 15.4%).
The fabricated crystalline silicon solar cell containing the silver nano particles exhibited higher electrical energy conversion efficiency compared with that of the solar cell fabricated from the conventional silver paste containing single micron particles [5].

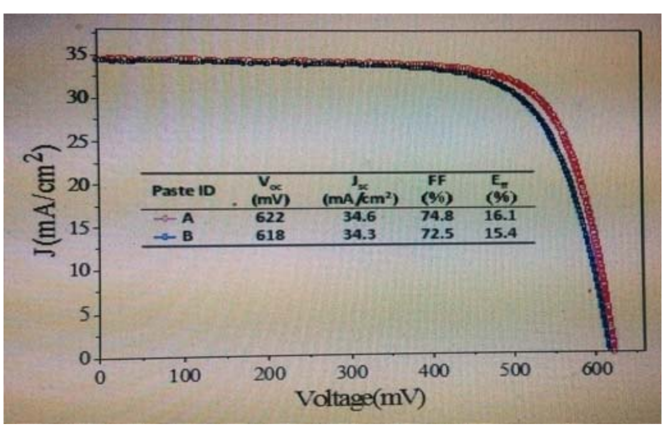

Fig-5: I-V performance of the fabricated crystalline silicon solar cells based on different silver pastes under AM 1.5 (1000W/ m^2).

8. CONCLUSIONS

It can be seen that the silver thick film fabricated resulting the silver paste containing silver nano particles exhibits denser structure (denser conducting network) than that of thick film based on silver paste containing single micron silver particles. The experimental results demonstrated that the silver nano particles, which were added as a sintering aid into the silver paste, promoted sintering of silver particles due to their unique nano effect.
The fabricated crystalline solar cells containing the silver nano particles exhibited higher electric conversion efficiency compared with that of the solar cell fabricated from the conventional silver paste containing single micron silver particles.
Therefore, this improvement should be attributed to the better thick film resulting from silver nano particles which not only improve the compactness of thick film, but also increase the line conductivity of silver electrodes.
It can be concluded that good front metallization contact can be achieved by using silver nano particles in the silver paste for highest efficiency of polycrystalline solar cell.

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