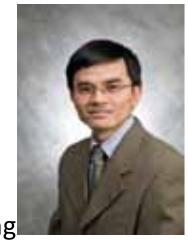
How Silver Paste Can Improve Silicon Solar Cell Performance/Cost Ratio



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Introduction:

The year 2009 was a nearly unprecedented period of extremes in the photovoltaic industry. During the 1st quarter, the so-called "Solar Winter", a phenomenon caused by the worldwide economic downturn in general and the Spanish market crash in particular, nearly shut down the solar power manufacturing industry. But the industry rebounded strongly, experiencing explosive growth in many segments during the third and fourth quarters of the year. Multiple marketing research firms confirmed that the silicon solar cell production volume in 2009 was more than 8 GW, with more than 50% growth over 2008. Almost all cell manufacturers were running at full capacity throughout the second half of 2009, and that trend has continued so far in 2010. The general outlook for the PV industry for 2010 is positive, even with the concerns over the German government cut of the feed-in tariff (FIT) starting in July 2010. Several major solar cell producers have announced plans for production capacity expansion. There is a growing consensus among these companies that the PV industry needs to graduate from government incentive programs and achieve grid parity in the normal utility markets as soon as possible. A few key players in this industry have already laid out their roadmaps, targeting a goal of $1 per watt at some point between 2012 and 2015. To reach this goal, solar cell manufacturers, material suppliers, and equipment vendors will have to align their efforts and cooperate with one another like never before.

Heraeus, a leading global precious metals management and materials supplier, applies its innovative technology and broad formulating experience to the photovoltaic industry. The company develops and supplies high-performance, high-quality silver pastes for crystalline silicon solar cells. The quality and performance of silver paste has a profound impact on the silicon solar cell's performance-to-cost ratio, a topic that is addressed in detail in this paper. Heraeus is dedicated to helping the PV industry achieve grid parity by developing and offering higher performance metallization solutions to our customers.

Silver paste fundamentals:

There are some similarities between silver paste for silicon solar cells and for traditional thick film applications such as hybrid circuits. The components of the paste, manufacturing process, and even some application processes, such as screen-printing, are fairly similar.

What is silver (Ag) paste? Paste is a uniformly dispersed mixture with multiple inorganic and organic components (see Figure 1). Since paste needs to be applied onto wafers by either screen-printing or other deposition methods, organic compounds serve as a temporary carrier, which accounts for the viscous nature of the paste. Those organic compounds will be evaporated and burned out during the drying/firing step and leave inorganic compounds on the wafers. Each element in the paste has its own function. For instance, Ag powder provides conductivity and glass helps penetrate antireflective layers, but it is the systematic combination of all functional elements that differentiates the performance of one paste from another. High-performance, high-quality silver paste should offer features such as good printability, fine line and high aspect ratio, screen life, solderability, a processing window, etc., as well as good electrical and mechanical properties such as high efficiency and reliability.

Factors that affect Si Solar cell efficiency:

Although the theoretical efficiency of a Si solar cell is close to 29%, and up to 24.7% on mono crystalline cells is achieved in labs, most production screen-printing cells today are running at ~18% efficiency for mono crystalline cells and ~16.3% for multi crystalline cells. The structure of a production cell, shown in Figure 2, looks simple. Many factors, however, from both the material side and processing side, can significantly affect cell efficiency. Base Si wafer quality, which is usually quantified by Minority Carrier Lifetime, passivation quality and Back-Surface Field quality have a direct impact on Open Circuit Voltage (Voc). Surface texturing quality, anti-reflectance layer quality and emitter quality are the major driving forces for Short Circuit Current (Isc). While both Voc and Isc are limited by minority carrier recombination, Fill Factor (FF) is the direct indicator of paste contact quality.

Figure 3, originally published in 2004[1], shows the loss mechanism in screen-printing (SP) production cells compared with photolithography (PL) lab cells. Although Si solar cell production technology, products, and processes - in particular screen-printing and pastes - have been improved greatly, it is still true that major efficiency loss results from metallization pastes contact quality, grid shading (reflectance), and poor short wavelength response. The direct impact on efficiency loss from metallization (SP to PL) is roughly 1%; the other 0.7% is also more or less limited by metallization paste. It is clear that the quality and performance of metallization paste play a critical role on the path toward improving Si solar cell efficiency.

The differentiators of Silver paste for Si Solar cell:

Contact Resistance:

One of the unique processing steps for silicon solar cells that poses a significant challenge for silver paste is called "spike firing". Within a few seconds of reaching 600 °C, silver paste needs to fire through the antireflective layer (normally SiNx:H layer at about 70 nm) to make as low as possible contact with the silicon without shunting the N/P junction, which lies only a few tenths of a micron underneath (Figure 4). The paste's low contact resistance remains one of the most important differentiating factors among the commercially available silver pastes for N+ contact in the market today.

Figure 5 shows paste A (left) and paste B (right) fired on the same wafer under the same firing profile. The difference in the interface between the Ag conductor and Si wafer is noticeable; paste A has a thick glass interface, while the interface glass layer is thin for most of the area of paste B. The result is that paste A has almost double the contact resistance of paste B. Heraeus silver paste SOL9235H, due to its unique chemistry, provides one of the lowest contact resistance measurements in the industry. This results in the highest fill factor of cells, on a wide range of sheet resistance emitters (from 50 to 80 ohm/sq).

Line Conductivity:

Although contact resistance is the key part of series resistance (Rs) of the cell, finger line resistance cannot be ignored. A few trends currently in the industry - such as three busbar design, double printing, and two steps of metallization - are aimed at improving finger line conductivity. A well-formulated silver paste could have almost 50% higher conductivity compared to other pastes. Figure 6 shows a relatively porous microstructure of fired Ag finger cross section on the left, while on the right the finger is much denser, which provides a base for better conductivity.

Double printing technology is currently a hot topic because of the potential for efficiency gain (theoretically as high as 0.5%), printer alignment accuracy improvement, and metallization paste progression. Another benefit is the de-link paste for finger line and busbar, which allows the application of non-etching paste on the busbar only as a means to minimizing recombination underneath the busbar area. A few mV improvement on Voc has been demonstrated.[(2)] Heraeus is offering a special paste - CL80-9381 - for the 2nd layer and busbar application to help customers take advantage of double printing technology. Using a combination of SOL9235H (1st layer) and CL80-9381 (2nd layer), 60umx25um finger lines can be achieved with another 30% increase of finger line conductivity (Figure 7).

Finger Aspect Ratio:

Due to the complex nature of double printing and much tighter requirements on printers and screens, PV cell manufacturers still prefer single print with a target of high aspect ratio. The ability to achieve higher aspect ratio finger lines is another factor that differentiates the commercially available silver pastes in the market today. Figure 8 shows a comparison of finger lines between Heraeus silver paste SOL9235H (Figure 8a) and a non-Heraeus silver paste (Figure 8b). The morphology is significantly different, with SOL9235H offering narrower, but taller, finger lines. This is another key benefit of SOL9235H; it delivers higher current density of cells due to reduced shading from fingers and lower series resistance.

Since screen-printing does not necessarily lend itself to high aspect ratio lines, the impact of screen quality to paste transfer and final print on cells is significant, but unfortunately often ignored in the industry. A screen with poor exposure quality (either overexposed or underexposed) often has rough edges of the opening and/or "clogs" as shown in Figure 9. It would not be surprising to see breaks on these cells due to the screen clogs.

Adhesion Strength:

Adhesion of silver paste on silicon solar cells is getting more attention in the PV industry today because module manufacturers are offering 25-year warranties on their modules. The ability to make good on that warranty depends in large part on the materials used to make it; and paste adhesion is a significant factor in helping to extend the lifetime of cells. Although there is no industry standard for adhesion testing, pull strength and failure mode are usually two differentiators for silver paste. Soldering methods (IR, Hot air or others) and profiles, ribbon types, as well as flux types all affect solderability and the adhesion of paste. From a silver paste formulation standpoint, we saw a strong link between paste composition and adhesion (Figure 10). The failure mode of Ag/Si interface after a pull test remains an area of debate [3]. Generally speaking, engineers would like to avoid the "cratering" defect (large chunks of Si were pulled out, as shown in Figure 11) after an adhesion test, due to the concern about possible micro cracks underneath the busbar after firing and soldering. A so-called cohesive failure mode, i.e. the failure that happens inside Ag paste (Figure 12), is preferred in the PV industry. Heraeus has specially designed and provided high adhesion strength with cohesive failure mode silver paste SOL9235HS to help our customers meet high reliability requirements.

Firing Window:

A wider processing window is one of the key features that cell manufacturers want. Since the actual temperature of a wafer during firing will be influenced by wafer thickness, AR coating uniformity, and emitter uniformity, as well as furnace temperature fluctuation, each wafer will see quite large variations in temperature. This is one of the reasons that production lines today still see significant variation in efficiency. The ability of Ag paste to maintain good contact without shunting cells in a wide range of firing temperature is another key factor. SOL9235H has proven, in many actual customer production lines, that it maintains a high efficiency during wider temperature processing windows than competitive paste (Figure 13). The feedback from the field supports the results of our internal study on the impact of firing furnace belt speed (and thus firing profiles) on cell efficiency as shown in Figure 14. In this study, the furnace temperature for all zones was the same; only belt speed was changed from 6,000 to 7,200 mm/min. This test demonstrated the performance robustness of SOL9235H under different firing profiles.

The benefit of efficiency gain from silver paste

Cell efficiency improvement in the Si PV industry is roughly 0.5% per year. The contribution from the metallization paste side, in particular front side silver paste, is well recognized. In the

2nd quarter of 2009, Heraeus introduced its flagship silver paste, SOL9235H, to the silicon PV market. The financial benefit to customers who adopt Heraeus paste into their production line has been significant. As shown in Figure 15, our customers saw a 0.2% to 0.4% efficiency gain with SOL9235H over other silver pastes on both multi crystalline and mono crystalline cells. Assuming a sale price for cells of $1 per W, this translates into a 6%-12% cost saving per cell.

Innovations by Heraeus, in both its technology and products, will not stop at SOL9235H. Heraeus develops and delivers 3-4 new silver pastes per year, helping the PV industry increase cell efficiencies and output using current technologies, as well as new designs and structures. Each of these pastes can be manufactured at the company's worldwide production sites in large lot volumes. Heraeus has recently introduced SOL9383 silver paste to the market for N type cell P+ contact application, which will help customers achieve cell efficiency close to 19%. Later in 2010, we will introduce new front side contact pastes for conventional cells. The new pastes are specially designed and formulated to make excellent contact on higher sheet resistance emitters up to 100 ohm/sq, while taking advantage of higher current density and open circuit voltage (Figure 16). We expect that the new pastes will further increase our customers' cell performance/cost ratio, a commitment we made to PV industry when we first entered it.

Heraeus, as the leading materials developer and supplier, is working closely with its customers and partners to help the PV industry achieve grid parity. We have set up fully functional technical application labs in Asia (Shanghai and Taipei), Europe (Hanau, Germany), and the US (W. Conshohocken, PA) to better serve our customers worldwide. We believe continuous evolution, innovation, and collaboration are the keys to the future success of PV.

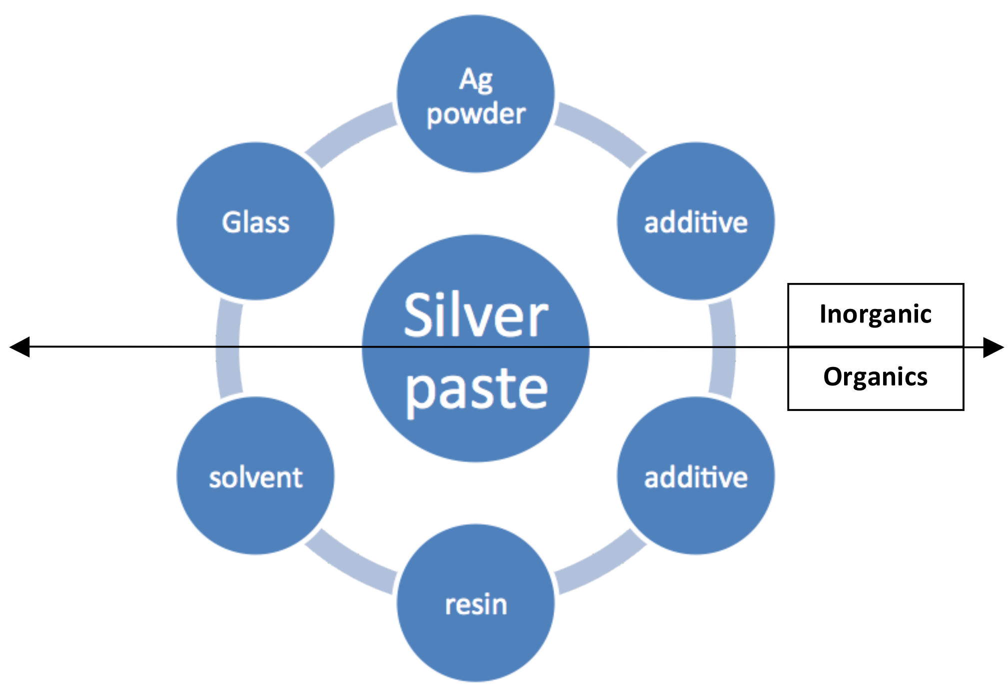


Fig. 1: Simplified composition tree of silver paste

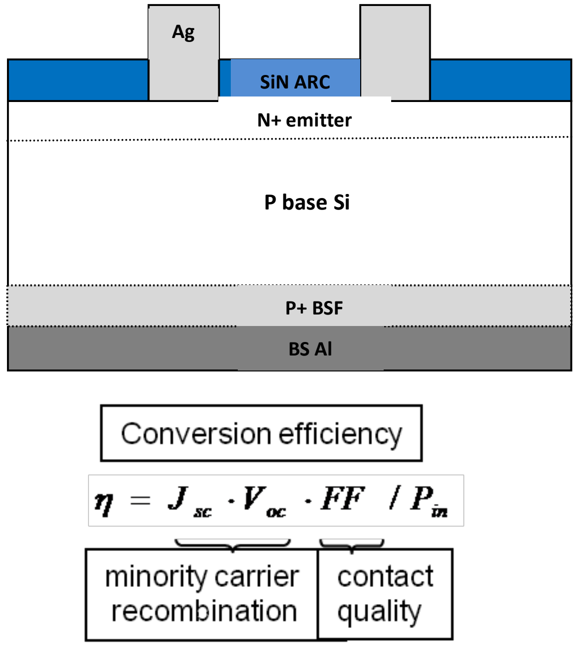


Fig. 2: Schematic of traditional Si solar cell and efficiency equation

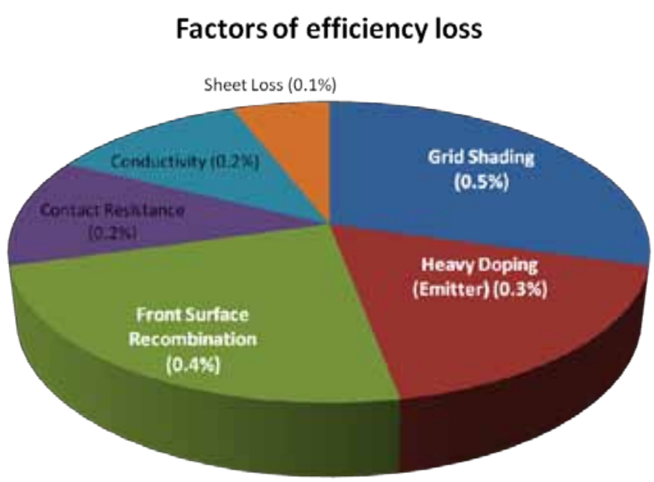


Fig. 3: Loss factors in screen-printing Si solar cells

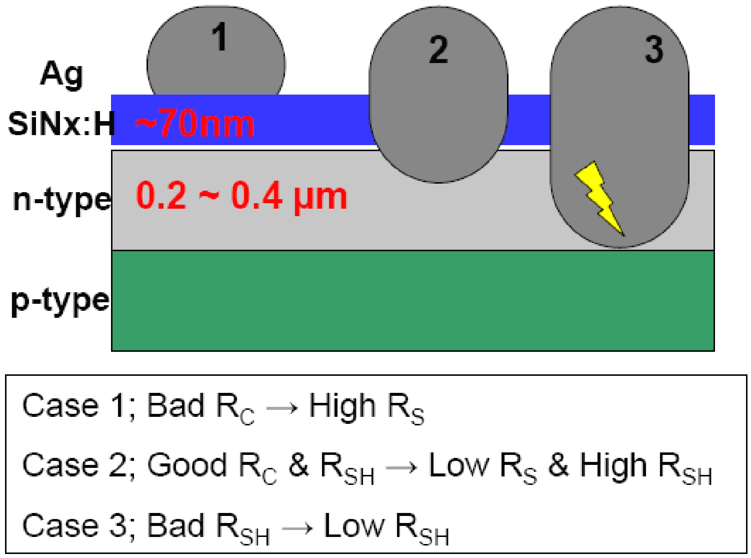
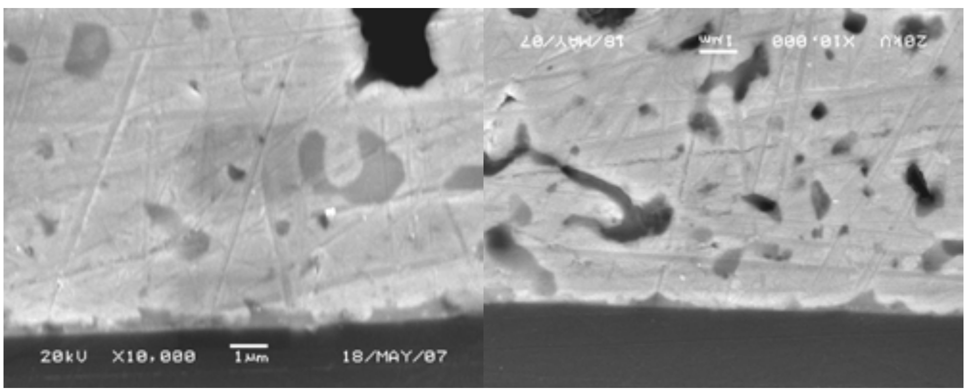


Fig. 4: Making good contact without shunting



Paste A Paste B

Fig.5: Thick glass interface (paste A) and thin glass interface (paste B)

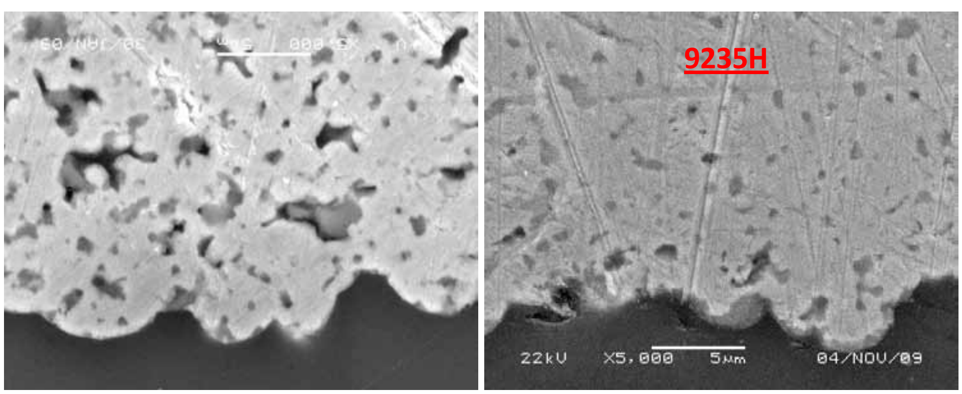


Fig. 6: SEM cross section of porous and dense finger line

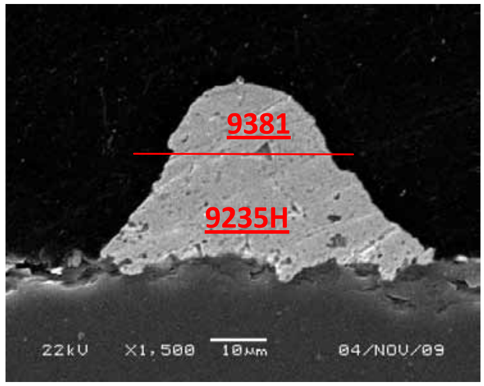


Fig. 7: SEM cross-section of double printing finger line

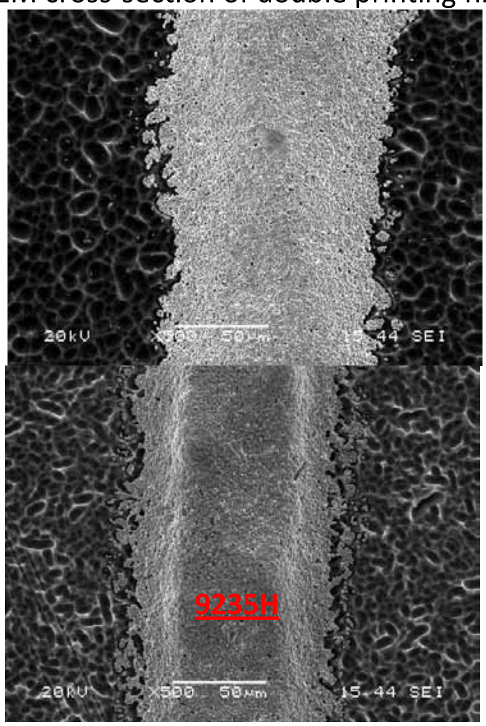


Fig. 8: Higher aspect ratio of Heraeus SOL9235H

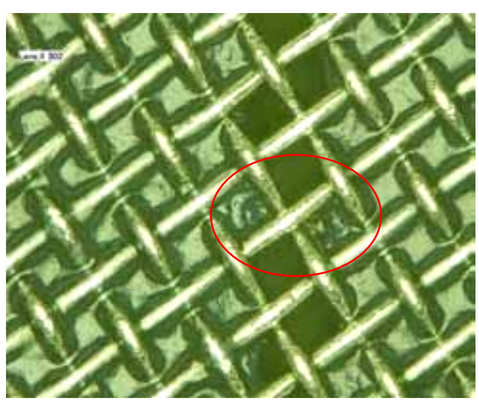


Fig. 9: New screen with “clogs” on opening

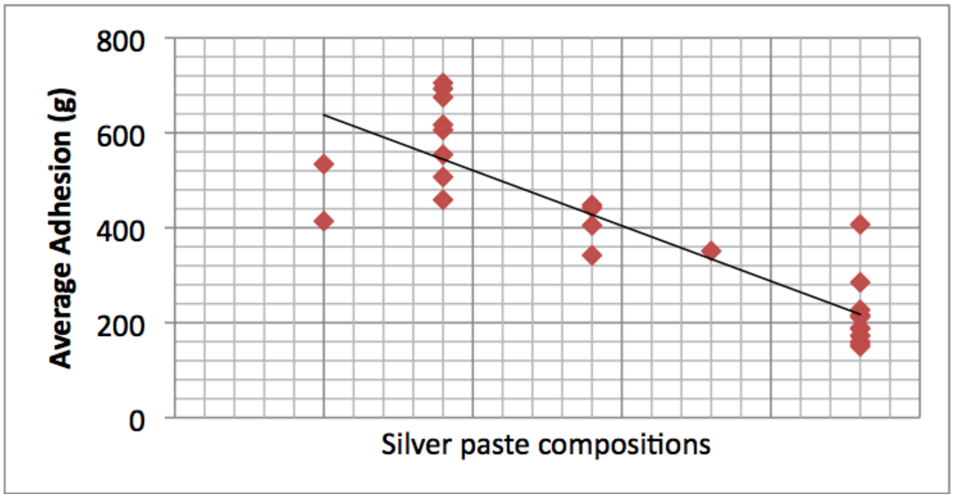


Fig. 10: The relationship of paste composition to paste adhesion

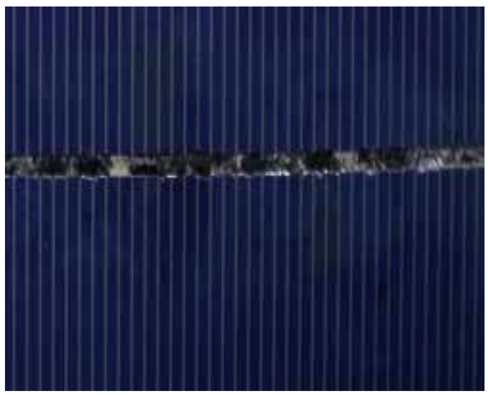


Fig. 11: Adhesive failure of Ag/Si interface

Fig. 12: Cohesive failure of Ag/Si interface

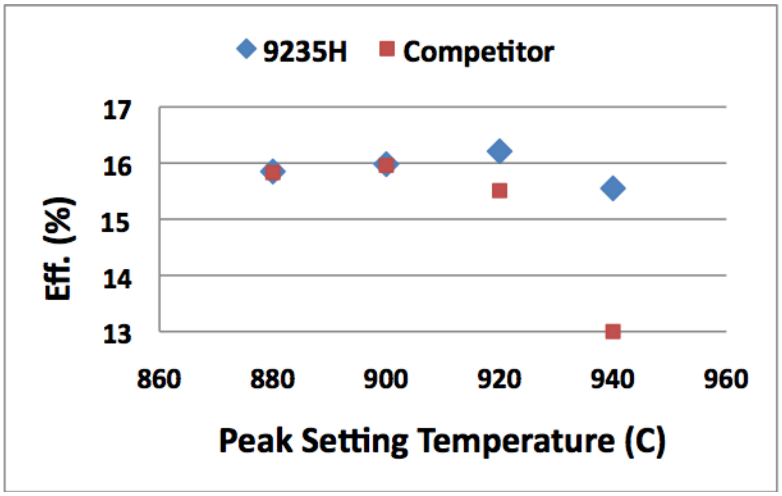


Fig. 13: Wider processing window of SOL9235H

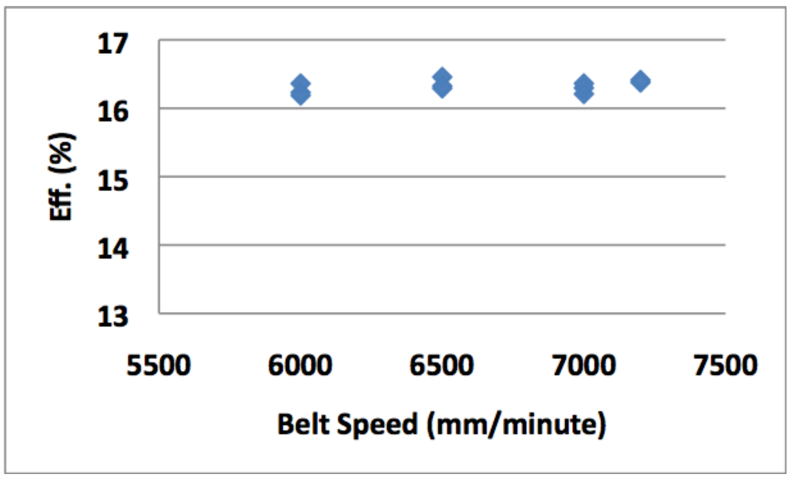


Fig. 14: Belt speed's impact on cell efficiency with SOL9235H

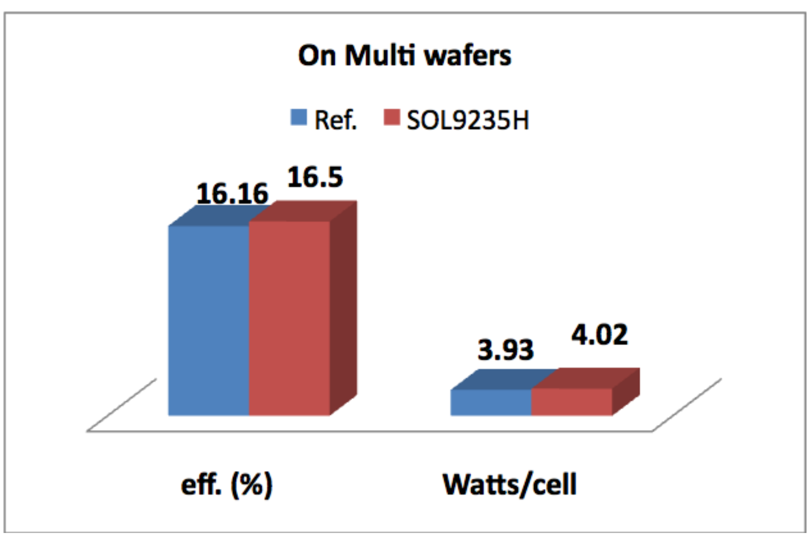


Fig. 15: Cell performance gain from SOL9235H

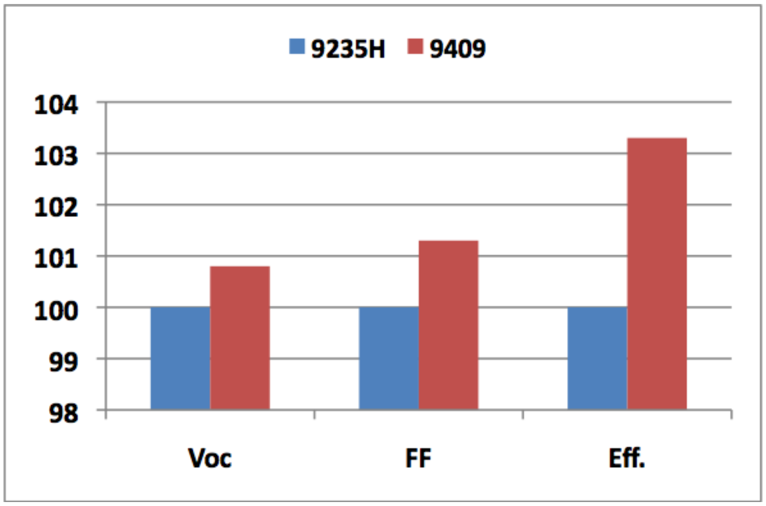


Fig. 15: New generation silver paste SOL94xx performance on 100 ohm/sq emitter

References:

(1): M.M. Hilali, A. Rohatgi and B. To; "A review and understanding of screen-printed contacts and selective-emitter formation"; Proc. Of the 14th Workshop on Crystalline Silicon Solar Cells and Modules (2004)

(2): T. Pham and W. Zhang, "Improving electrical performance by double print method and non contact busbar design"; submit to 25th EU PVSEC (2010)

(3): J. Moyer and W. Zhang, "The role of silver contact paste on reliable connectivity systems"; submit to 25th EU PVSEC (2010)