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FURTHER PROGRESS IN METAL AEROSOL JET PRINTING FOR FRONT SIDE METALLIZATION OF SILICON SOLAR CELLS

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ABSTRACT:
Front side contacts on silicon solar cells were printed with a metal aerosol jet system using highly solid loaded silver inks exceeding 70 wt%. The printed, fired and plated fingers covers only 70% of the area of a screen-printed contact; at the same time the line conductivity is improved due to followed light induced plating step. The requirements for an aerosol ink were determined and an ink was formulated. The ink was successively improved to extend the machine uptime, to decrease the printed line width and to increase the printing speed. Additionally a commercially available screen print paste was modified for aerosol printing. Line widths below 50 µm using a diluted screen print ink and line width below 20 µm and machine uptimes of more than 10 hours are possible using a new ink formulation. The minimum amount of silver ink which is necessary to process a front side contact, electrically and mechanically, was determined. The contacts were analyzed, and solar cells were processed on monocrystalline and multicrystalline material. The new formulated aerosol ink was tested on 15.6 cm x 15.6 cm mc Si solar cells, achieving efficiencies up to 16.5%. Using a diluted commercially available screen print paste 12.5 cm x 12.5 cm Cz Si cells with an aluminum back surface field were processed, achieving energy conversion efficiencies up to 18.3% .

KEYWORDS: metallization, aerosol printing, fine line printing, light-induced plating

Introduction

Researchers as well as manufacturers are looking intensively for new industrial processes to reduce cost per watt of silicon solar cells. This can be achieved either by increasing the cell efficiency or by reducing material and production costs. Currently cell efficiencies of more than 24% have been achieved. However, this laboratory process includes several extravagant process steps like photolithography which is not economic for an industrial application, yet. To close the gap in efficiency between industrial cells and high-efficiency concepts, new processing methods are necessary. Especially the metallization that distinguishes an industrial cell from a high-efficiency cell. For the rearside, high-efficiency concepts as e.g. the laser fired contacts (LFC) [1], are currently transferred into industry. The front side metallization step holds one of the main potential for further increase of efficiency. An optimized front contact as it is used in high-efficiency concepts consists of a successive evaporation of titanium, palladium and silver defined by photo-lithography. These contacts have only a width of a few micrometers whereas conventional screen-printing produces fingers with a width of 120 µm covering 7 to 8% of the cell’s surface. The front side contact can be improved by reducing the contact resistance, the series resistance and the contact area.
Our approach is based on a two-layer process. This implies the great advantage that both layers can be optimized individually. In a first step, a thin line with a low contact resistance and a good mechanical adhesion is formed and thickened in a second step using light-induced plating (LIP) [2]to increase conductivity in the finger. For example the specific line resistance for a plated contact is about 1.9 x 10^{-8} Ωm compared to 3.2 x 10^{-8} Ωm of a screen printed contact.

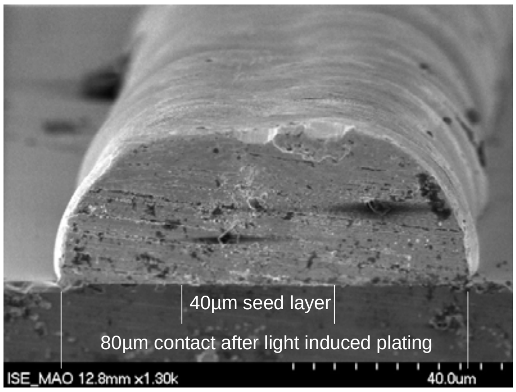

Figure 1: Cross section of an aerosol printed, fired and plated contact finger. About 20 µm of silver is plated on top of the seed layer. The height of the seed layer is about 1.5 µm.

At Fraunhofer ISE different technologies are currently under investigation to deposit the seed layer [3]. Also a wide range of different printing systems is available. The seed layer for example can be printed by fine line screen printing, stencil printing, pad printing or ink jet printing. A very promising alternative to create the seed layer on silicon solar cells is metal aerosol jet printing [4], which is a contactless and maskless deposition technique. A cross section of an aerosol printed and plated finger is illustrated in Figure 1. The aerosol printed seed layer is approximately 40 µm wide and has a height of only 1.5 µm.

The current transport occurs by the light induced plated silver layer which covers the seed layer and build the contact up to 20 µm height and 80 µm width.

Metal aerosol jet printer

The metal aerosol printer is a Maskless Mesoscale Material Deposition ($M^3D^{®}$) system from Optomec® INC., USA [5]. The system is designed for non contact printing of electronic features in the range of 10 µm to 100 µm. The deposition of material is a two step procedure. Intitially an aerosol is created either by pneumatic atomization or by ultrasonic atomization. The utilized atomization technique depends on the ink parameters. Inks with a low viscosity η_d<10 mPas and a small particle size distribution d_{50}<50 nm can be ultrasonically atomized. The pneumatic atomizer, the working principle is illustrated in Figure 2, is used for slurries with viscosities up to 1000 mPa. In case of pneumatic atomization an additional device, a so called virtual impactor is necessary to concentrate the aerosol. About 95% of the gas stream which is used to create the aerosol is separated from the mist inside the virtual impactor. The remaining concentrated and condensed aerosol is forwarded into the deposition head, Figure 3.

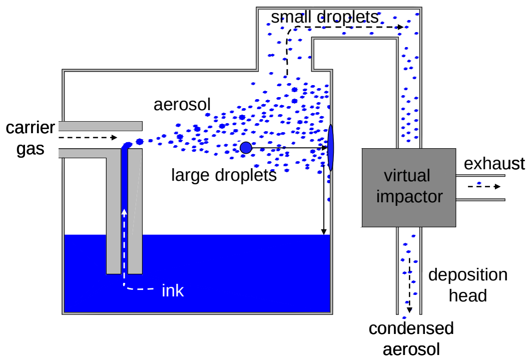

Figure 2: Working principle of the pneumatic atomizer including the virtual impactor. Only smaller droplets are transported by the carrier gas whereas larger droplets remain in the ink jar.

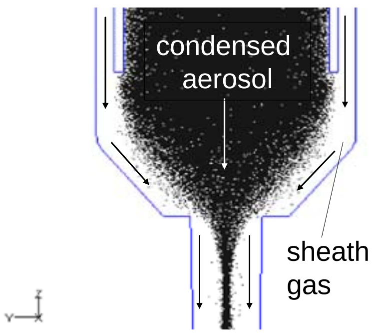

Figure 3: Simulation of the gas flow in the deposition head. A droplet size of d_{drop}=1 µm an N_2 as process gas was assumed.

Inside the deposition head the condensed aerosol is focused and forwarded into the nozzle. The technique is based on a principle which is used in optical aerosol particle counters [6]. It consists of two interconnected tubes ending on top of a nozzle.

The aerosol comes through the inner tube with a low velocity. A second gas stream, called sheath air, flows laminar in the outer tube with a higher velocity. On top of the nozzle, the outer gas surrounds the aerosol and streams through the nozzle. The sheath gas prevents the aerosol from getting into touch with the wall and focuses it. As a result, a narrow and dense aerosol jet exits the tip and is deposited as a thin line on the substrate. The line width can be influenced by the ratio of sheath gas flow to condensed aerosol flow. Narrow lines can be printed using an optimized ratio of the gas flows. If the sheath gas rates are getting too high, no significant change in line width is observed. On the contrary, the aerodynamic behavior of the gas streams changes and sheath gas and aerosol are mixed. The result is a wide sprayed line of low density. Another option to adjust the line width is the nozzle diameter. A set of nozzles with openings between 100 µm and 300 µm are available. Depending on the ink the line width can be up to 10 times smaller than the nozzle opening. Line width below 20 µm were achieved, using a highly silver loaded aerosol ink (w>70 wt%) and a 100 µm nozzle (see Figure **4**).

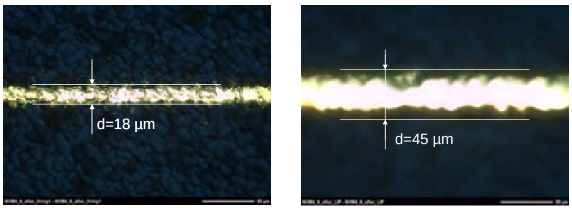

Figure 4: Aerosol printed finger width of d=18 µm, after firing (left) and d=45 µm after LIP (right)

Ink requirements

The deposited seed layer should provide both, a good mechanical adhesion and a good electrical contact. If solar cells with an antireflection coating are contacted, the ink additionally has to penetrate through the SiN_x layer. Thick film silver pastes with glass frits fulfill these requirements. However, they are too viscous for aerosol printing and can not be used directly. An aerosol ink needs a lower viscosity, preferable η_d <1 Pas and a reduced particle size distribution. If a screen-printing paste is used, it has to be diluted.

Currently there is no commercial ink available which is optimized for aerosol printing and which can be used as a seed layer for front side contacts on silicon solar cells. First promising results could be achieved using commercially available screen-print paste which is used in a standard production process. Such a paste has solid loads up to 80 wt.% and viscosity's higher than 10 Pas. To transfer this screen-print paste into an aerosol ink, it has to be diluted to reduce the dynamic viscosity below η<1 Pas. The solid load drops due to the dilution from 80 wt.% to approximately 60 wt%. After printing, the solid load of the deposited material drops again to 40 wt%. The atomization in the pneumatic nebulizer is responsible for the additional dilution during printing. The atomizer separates the ink in larger and smaller particles. Large droplets and rather large particles are atomized against the wall of the jar and remain in the ink vessel, whereas smaller droplets, loaded with smaller particles are carried by the gas flow towards the deposition head, see Figure 2.

To find the optimum particle size for a highly silver loaded aerosol ink, a diluted screen-print paste (ink A) with a wide particle size distribution and a second paste (ink B) with a narrower and smaller particle size distribution was analyzed in a laser particle analyzer before and after printing. The size distribution of the original ink A contains particles from below 100 nm up to diameters of more than 6 µm. However, the printed and deposited material contains only particles smaller than 2 µm with an average particle size around d=500 nm. Only small particles are atomized whereas large particles remain in the ink vessel. If ink B with an original particle size below 1 µm is atomized, no separation in particle size and no decrease in solid load during printing were observed. The solid load of ink B was 55 wt% before and after printing and the size distribution remains constant with an average value at d= 250 nm; (Figure 5 and Figure 6).

A narrower particle size distribution and the use of more mono-disperse particles causing a homogeneous aerosol generation and a constant material deposition. Both have a beneficial effect on the system. In this way the system uptime could be increased to more than 10 hours at a higher material deposition rate. A higher deposition rate leads to a higher printing speed, which could be increased from v=20 mm/s to v=50 mm/s. At the same time smaller nozzle outlet diameters can be used and line width below 20 µm can be printed.

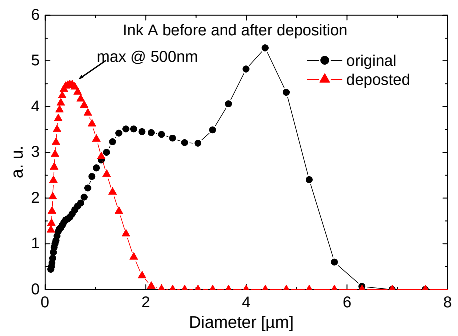

Figure 5: Particle size distribution of a conventional screen-print paste. The size distribution after printing is shifted towards particle sizes below 2 µm.

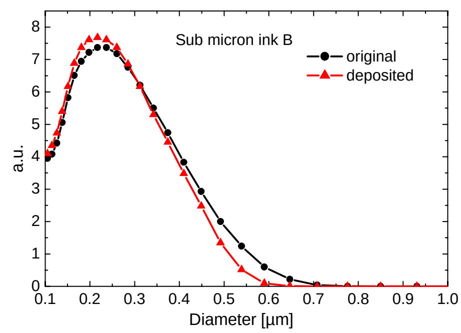

Figure 6: Particle size distribution of a paste suitable for aerosol printing. The distribution is constant – no separation in small and large particles is taking place during printing process.

Printed, fired and plated contacts

The formation of a conducting seed layer requires a certain amount of material, or a certain contact height respectively.

The necessary contact height was determined for a diluted screen print ink and a aerosol ink. Different contact heights can be printed either by varying the aerosol flow or by multiple printing. Structures from 1 µm up to 15 µm have been processed by multiple printing. The contact width was almost kept constant at 50 µm. It was found, that for both inks a height of only 1-2 µm is necessary to penetrate through the antireflection coating, to achieve sufficient adhesion and to form a good electrical contact. Independent of the contact height a contact resistivity between ρ_c=5 mΩ cm² and ρ_c=8 mΩ cm² was measured to an emitter with a sheet resistance of about 60 Ω/sq, which is comparable to a screen-printed contact. Assuming a printed contact width of 40 µm and a height of 1.5 µm about 30 times less silver material is consumed compared to a screen-printed contact.

The printed cells are fired in a standard fast firing belt furnace at 880°C. The contact shrinks due to the evaporation of solvents and binders and due to the sintering of the silver particles. The single silver particles are sintering into clusters and islands and forming a interrupted conducting layer, hence the line conductivity is by far too low.

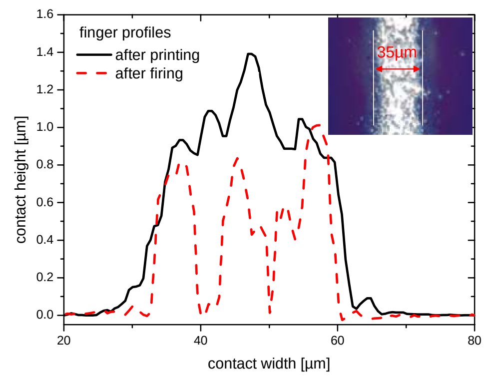

Figure 7: Cross section of a printed (solid line) and fired contact (dashed line). The small picture shows a top view of an aerosol printed and fired contact.

The seed layer needs to be plated in the second contact forming step. During LIP, silver grows isotropically and also closes gaps between the sintered silver particles and forms a dense highly conductive silver layer, compare Figure 1. The contact changes its shape from a flat seed layer into a contact of a half circular shape with an aspect ratio (height:width) of 1:3 -1:5 depending on the seed layer width and plating height. Additionally the contact resistance is reduced because of further current paths between silver crystallites and LIP silver [7].

Solar cell results

Multicrystalline 15.6 cm x 15.6 cm silicon solar cells were industrially preprocessed at Q-Cells including wet chemical texturing, emitter diffusion, SiN_x antireflection coating and screen printing of the rearside. The emitter sheet resistance of the cells was about 55 Ω/sq.

The front contact was formed in a three step process, metal aerosol jet seed layer printing, inline co firing and light induced plating.
For aerosol printing an optimized ink, containing small particles, having a reduced viscosity and a high solid load of w=70 wt%, was used to print the front side grid. Assuming 70 µm wide contact fingers, an emitter sheet resistance of 55 Ω/sq and a contact resistivity of ρ_c=1 mΩ cm², an optimal finger separation distance of 2 mm was calculated. After printing the front side contacts, the cells were fired in an in-line fast firing furnace at set temperatures between 800°C and 940°C. The optimum firing temperature for an aerosol ink was found to be in the range of 870°C to 900°C. During aerosol printing, parameters like printing speed, deposition rate and gas flow rates were kept constant, resulting in a dense, about 40 µm broad line. After firing the line width decreases to about 38 µm. During LIP approximately 15 µm of silver is plated resulting in a 60-70 µm wide contact. 79 fingers of a width of 70 µm together with 2 busbars, each 1.5 mm wide, resulting in a metallized and shaded solar cell area of 4.5%. Reference cells were screen-printed on the same material and also co-fired in an in-line fast firing furnace. The screen printed cells having a shaded area of 6.5%.
The 2% lower shading loss of aerosol printed cells results in a 2% higher j_{sc} value. IV-parameters of aerosol and screen-printed multicrystalline solar cells are presented in Table 1.

	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	$R_{S\ light}$ [Ωcm²]	η [%]
aerosol print +LIP	79 Fingers with a finger width of 70µm				
best cell	615	34.3	78.2	0.75	16.5
Ave/50	613	34.2	77.5	0.82	16.2
Screen print	65 fingers with a finger width of 100µm				
best cell	614	33.8	78.0	n.a.	16.2
Ave/10	609	33.5	75.3	n.a.	15.5

Table 1: IV-parameters of 15.6 cm x 15.6 cm mc-Si solar cells. Best cell values and average values for aerosol jet printed + LIP contacts and screen printed contacts..

In a further experiment monocrystalline silicon solar cells were produced at Fraunhofer ISE on 12.5 cm x 12.5 cm, 1 Ω cm, boron doped Cz-silicon wafers. The cell surface is textured and coated by a sputtered SiN_x antireflection coating. The emitter sheet resistance is 45 Ω/sq. The rear side was conventionally screen-printed. The front side contacts were aerosol printed, using a diluted screen print paste. The printed fingers had a width of approximately 100 µm. After firing in a fast firing furnace the contacts were thickened by LIP up to a line width of 120 µm. The cells were edge isolated by laser scribing and breaking. The metallized area is similar to screen printed contacts. However, the height of the seed layer is only 1-2 µm, the current transport occurs mainly via the plated silver which results in a lower line resistance. IV-parameters are summarized in Table 2, confirming the high potential of the two layer metallization process. Efficiencies as high as 18.3% and fill factors of 81% were achieved.

front side metallization	Voc [mV]	Jsc [mA/cm²]	FF [%]	η [%]
metal aerosol jet + LIP + annealing	624	36.1	81.0	18.3

Table 2: IV-parameters of aerosol printed + plated Cz Si solar cells with. The seed layer was printed using a diluted commercial available screen-print paste.

Conclusion

Metal aerosol jet printing is demonstrated to be a reliable technique to create a seed layer for the front side contacts of silicon solar cells. The seed layer provides a good electrical contact and a good mechanical adhesion. Using a diluted screen print paste, on Cz Si, efficiencies of 18.3% are realized, demonstrating the high potential of a two layer process. An ink for aerosol printing was successively developed in close cooperation with Ferro and successfully tested on multicrystalline silicon solar cells. Energy conversion efficiencies up to 16.5% on large area mc solar cells were achieved. Fine line printing, below d=20 µm is possible, however the cell performance is limited due to a too high contact resistance. To derive benefit from a reduced contact area further work will focus on a reduced contact resistance.

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