

## IMPROVED FRONT SIDE METALLIZATION BY AEROSOL JET PRINTING OF HOTMELT INKS

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### ABSTRACT

The rheology of a low viscous aerosol ink was modified into a hot melt ink by substituting the original solvent system by a thermo plastic alcohol. Additionally the aerosol printer was adapted to hot melt printing by heating all parts which are in contact with the ink, including the atomizer, virtual impactor, printing head and atomization gas. Front side contacts on silicon solar cells were printed with a metal aerosol jet printer using this hotmelt ink. Improved line resolution, higher aspect ratio and higher solid content compared to conventional aerosol inks could be achieved. To demonstrate the industrial feasibility, a multi-nozzle printing system was used. Line widths of 40  $\mu\text{m}$  could be achieved. The aspect ratio of the fingers is increased from 1:40 to 1:6. Large-area multicrystalline silicon solar cells were, printed at room temperature at different printing speeds, fired in an in-line belt furnace and finally plated in an industrial plating machine. Energy conversion rates as high as 16.1% were achieved. The short-circuit current and the fill factor of these cells is around 34  $\text{mA}/\text{cm}^2$  and 78%, respectively, showing the excellent contact geometry of the fabricated fingers.

**KEYWORDS:** metallization, aerosol jet printing, fine line printing, hot melt printing, light-induced plating, silicon solar cells

### Introduction

Screen printing is currently the commonly used technique to create a front side metal grid of an industrial silicon solar cell. The technique is reliable, cheap, fast, and creates a contact in a single production step. However, the technique has its drawbacks like applying mechanical stress on the wafer during printing. Additionally the printed contacts being broad and shallow and due to the porous structure of the fired contact-paste the line conductivity is rather low. Metal aerosol jet printing [1, 2] in combination with light-induced plating (LIP) [3], is able to overcome these disadvantages. The printing technique is able to create fine line contacts of less than 20  $\mu\text{m}$  in width, without getting into touch with the wafer. The line conductivity and the thickness of the final contacts are determined by LIP. The plated silver has a much better conductivity compared to screen-printed silver which reduces the volume of the final contact. The two-layer metallization concepts of Fraunhofer ISE [4] take advantage of the possibility of an individual optimization of each layer. The mechanical and electrical contact properties are determined by the seed layer whereas the line conductivity is subsequently increased in a LIP step. On a 2x2  $\text{cm}^2$  Fz-Si solar cell with a passivated rear side and LFC contacts, we have recently achieved an efficiency of 20.3% [5]. This high efficiency was obtained by using a specific seed layer ink developed at Fraunhofer ISE which results in a low contact resistance  $\rho_c < 2 \text{ m}\Omega\text{cm}^2$  even on a high ohmic emitter  $R_{sh} = 110 \Omega/\text{sq}$ . Line widths below 20  $\mu\text{m}$  are possible using aerosol jet printing. However for fine line printing, especially on a textured surface, the substrate needs to be heated. The heating step influences the long term stability of the process and is difficult to implement in an industrial production. In this paper we demonstrate a possibility of fine line printing even at room temperature (RT).

The larger the ratio of contact height to contact width (aspect ratio), the better the contact properties in terms of shading losses and line conductivity. Screen-printed contacts achieving an aspect ratio of typically 1:10. This ratio can be improved if hotmelt paste is used. Dependent on the temperature the paste changes its viscosity. At high temperatures the paste becomes liquid whereas at room temperature the paste is solid. The wetting of the wafer by the paste and the aspect ratio can be controlled by temperature. The best cell result for screen-printed cells has been produced using hot melt technique [6].

In case of metal aerosol jet printing, the aspect ratio is mainly determined by the plated silver, however, the smaller the seed layer, the better the aspect ratio. For example, if the seed layer has a width of 40  $\mu\text{m}$  and a height of 1  $\mu\text{m}$  these leads to an aspect ratio of 1:40. Applying LIP, where silver grows isotropic on the seed layer, e.g 15  $\mu\text{m}$  in height and 30  $\mu\text{m}$  in width, the aspect ratio changes to more than 1:5. This value can be even more increased if the seed layer already has a better aspect ratio, either by reducing the width at a constant height or increasing the height at a constant width. If a hotmelt ink is used in a metal aerosol jet printer, both a thinner and higher contact can be printed. The seed layer height could be increased from 1  $\mu\text{m}$  to more than 7  $\mu\text{m}$ , keeping the width at a constant value of 40  $\mu\text{m}$ .

### Hotmelt aerosol inks

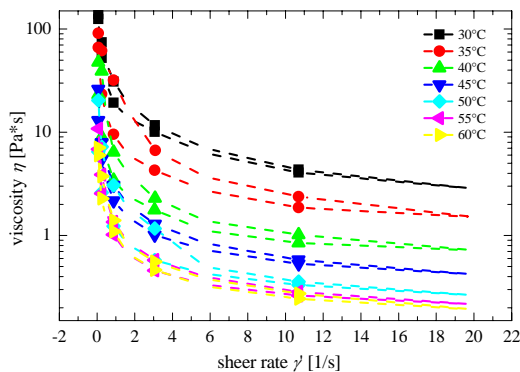
To create a fine contact line on a silicon solar cell, with a metal aerosol jet printer, the ink should meet the following requirements:

- Viscosity below 1 Pa\*s at low shear rates  $< 10 \text{ 1/s}$
- Particle size distribution below 0.5  $\mu\text{m}$
- Solid load of at least 65m%

The low viscosity and the small particle size distribution are determined by the pneumatic atomizer. Especially a low viscosity is necessary during atomization to create a dense and homogenous aerosol.

However, a low-viscous ink, deposited on a textured solar cell tends to wet the surface and leads to an increased line width. If narrow contacts of high aspect ratio are desired, the viscosity of the ink should be as high as possible. Till now, the problem was solved by heating the substrate up to a temperature of  $T=150^{\circ}\text{C}$ . During the deposition the solvent of the single ink-droplets is evaporated and the dried material sticks on the substrate as soon as it gets into contact with the hot surface. The contradiction of a low ink viscosity during atomization and high viscosity on the substrate can be overcome by using hotmelt inks.

To turn a conventional low viscous aerosol ink into a hotmelt ink, we partly substitute the solvent system by a thermo-plastic alcohol. As a thermo-plastic alcohol we used hexadecanol, which is solid at room temperature and has its melting point at  $T_{\text{mp}}=39^{\circ}\text{C}$ . The optimum amount of thermo-plastic alcohol was determined by mixing aerosol inks of different alcohol contents and measuring the viscosity at different temperatures. The ratio of solids (silver, glass) to organic (solvents, dispersant agents, thermo plastic) was kept constant 70:30 by weight. If too much of the thermo-plastic alcohol is added, the ink viscosity is too high to produce an aerosol even at temperatures of  $T>70^{\circ}\text{C}$ . On the contrary, if too little thermo-plastic alcohol is added the aerosol droplets condensate too slow and the ink keeps liquid and still wets the substrate.

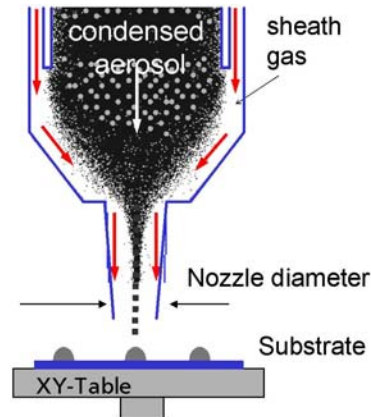


**Figure 1:** Rheology of a hotmelt aerosol ink, measured at different temperatures and shear rates. Next to the strong temperature dependence the ink shows a shear thinning behaviour.

The rheological behaviour of such a designed hotmelt ink is illustrated in Figure 1. Besides the temperature dependence, the ink also shows a shear thinning behaviour. This is typical for highly solid-loaded inks; in our case the ink contains 70 m% solids. A low viscosity at shear rates  $<10\text{ 1/s}$ , as it is necessary for a good atomization, can already be reached at a temperature of  $40^{\circ}\text{C}$ . The viscosity of the ink drops below the border of  $1\text{ Pa*s}$  and can be atomized like a conventional aerosol ink. The atomization rate can be controlled by the temperature. However, a temperature of more than  $70^{\circ}\text{C}$  leads over time to an evaporation of solvent and the ratio of solids:organic is changed. A long term stable process is possible at temperatures between  $40^{\circ}\text{C} - 60^{\circ}\text{C}$ . The lab-scale system which we are using it, illustrated in Figure 3, was running for several hours without changing the ink composition and viscosity.

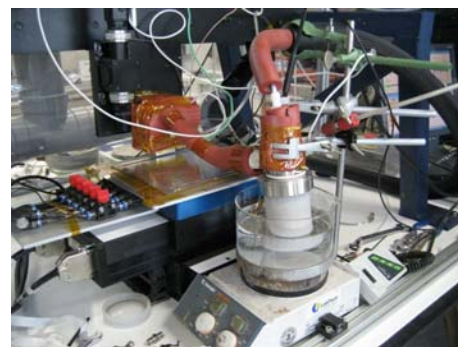
### Aerosol jet printer modified for hotmelt inks

The metal aerosol printer is a Maskless Mesoscale Material Deposition (M<sup>2</sup>D<sup>®</sup>) system from Optomec<sup>®</sup> Inc., USA [7]. The system is designed for non-contact printing of electronic features in the range of  $10\text{ }\mu\text{m}$  to  $100\text{ }\mu\text{m}$ . Fragile and uneven substrates can be contacted without the risk of breaking. The operation of the printer is based on an initial created aerosol which is forwarded into the deposition head where it is focused by a sheath gas and finally deposited on the substrate see Figure 2.



**Figure 2:** Aerosol flow inside the printing head. The aerosol droplets solidify as soon as they left the heated printing head and sticks on the unheated wafer.

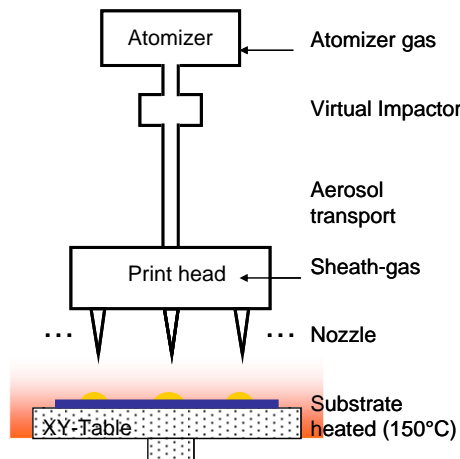
As the system is almost closed apart from the nozzle openings, it is easy to heat the system up to the required ink temperature and keep the temperature constant. The atomizer together with the ink is temperature-controlled by a water bath. All parts of the printer which are in contact with the ink, like virtual impactor, connecting tubes and the printing head, are wrapped with a heating wire, isolated and heated at a temperature of  $40^{\circ}\text{C} - 60^{\circ}\text{C}$ .



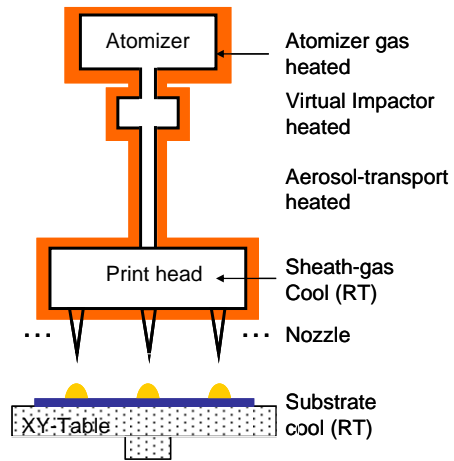
**Figure 3:** Picture of the 10-nozzle aerosol jet printer modified to print hotmelt inks.

In Figure 4 and Figure 5 a comparison of the two different operation modes, aerosol-jet and hotmelt aerosol-jet print can be seen. For the conventional aerosol print, the system is at RT and the substrate is heated. As the solvents used in aerosol inks having a high boiling point typically  $T>150^{\circ}\text{C}$  the substrate has to be heated up to this temperature to evaporate and dry the ink on the wafer.

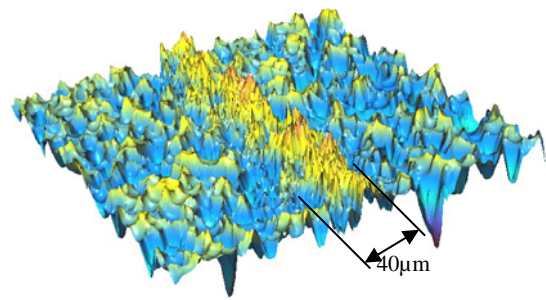
Solvent with lower boiling points are not applicable as the solvents would evaporate already during atomization and the ink viscosity would increase over time. Heating of the substrate is so far the only method to process narrow lines on a solar cell. However, for an industrial application a heated printing step causes many problems in particular at a high throughput. Figure 5 show the schematic drawing of a hotmelt aerosol system. With this setup it is possible to keep the wafer at RT. All parts of the system which are in contact with the ink or the aerosol are heated apart from the sheath gas which is at RT to cool down the ink droplets inside the nozzle and on their way to the wafer. As soon as the ink is in touch with the cold wafer, the ink condensate and a silver line can be built up without wetting the wafer. Depending on the aerosol output and the printing speed line heights of several  $\mu\text{m}$  are possible without changing the line width. In general, the line width is mainly dependent on the used nozzle diameter. Contact fingers below  $20\ \mu\text{m}$  are realized on textured solar cells [2]. The printed lines shown in Figure 6 and Figure 7 are printed with a  $200\ \mu\text{m}$  nozzle opening. The line width is for both systems  $40\ \mu\text{m}$ . However, if hotmelt ink is used, the height is increased from  $2\ \mu\text{m}$  to  $7\ \mu\text{m}$  after printing. After firing the line shrinks due to the evaporation of solvents and sintering of the silver and glass particles and the height is reduced to about  $1\ \mu\text{m}$  and  $3\text{--}4\ \mu\text{m}$ , respectively. In both cases the line conductivity is too low and plating or a second printing step of a high conductive ink is necessary. For a fired seed layer of only  $1\ \mu\text{m}$  in height, a value for the conductivity can not be determined because the layer is partly interrupted. In case of hotmelt ink where the seed height is still  $3\text{--}4\ \mu\text{m}$  after firing, a resistivity, can be measured of  $\rho=(5\text{--}8)\times 10^{-8}\ \Omega\text{m}$ . A conductive seed layer reduces the plating time and ensures homogenous plating. Additionally, a higher contact structure during firing also tends to form a lower contact resistance to the emitter layer [8].



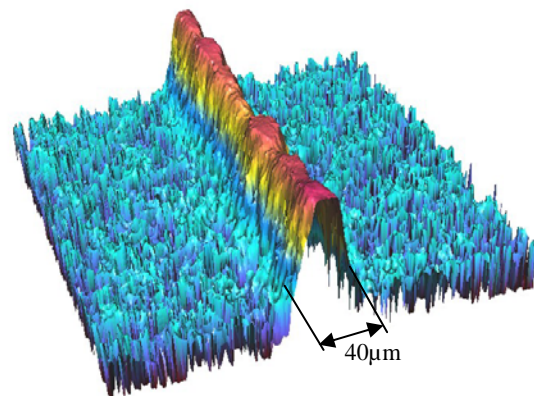
**Figure 4:** Schematic of the multi-nozzle printer for conventional aerosol jet printing. The printing system is at room temperature and the substrate is heated up to  $150\ ^\circ\text{C}$  to dry the ink.



**Figure 5:** Schematic of the printing system used for hotmelt printing. The printing system is heated up to  $60\ ^\circ\text{C}$  to keep the ink viscosity, inside the system low. The nozzle and the substrate are at RT to condensate the ink as soon as it exits the printer.



**Figure 6:** 3-D image of an aerosol printed contact using a conventional ink. The contact has a height of only  $1\text{--}2\ \mu\text{m}$ .



**Figure 7:** 3-D image of an aerosol printed contact using hotmelt ink. The width of the contact is again  $40\ \mu\text{m}$ , whereas the height is increased to  $7\ \mu\text{m}$ .

## Solar cell results

In order to test hotmelt aerosol jet printing as an industrially feasible printing application, 15.6×15.6 cm<sup>2</sup> mc-Silicon solar cells were produced. The cells have an emitter sheet resistance of  $R_{sh}=65 \Omega/\text{sq.}$ , an acid texturing and a silicon nitride antireflection coating. The rear side of the cells is screen-printed with aluminium paste and aluminium-silver paste for the tabs. The aerosol printed front contacts are produced at different printing speeds. The printing speed determines the line height and slightly the line width. For an industrial application, printing speeds of  $v>100 \text{ mm/s}$  are desirable. In our lab-type system, the printing speed is limited mainly by the system itself. The single atomizer we are using, is not able to generate a sufficient amount of aerosol to deposit a dense line at a printing speed of more than 25 mm/s. Lines printed at a speed of  $v=30 \text{ mm/s}$  or more are too thin and partly interrupted after silver plating. All solar cells, processed at lower printing speeds (between 5 mm/s and 25 mm/s) show quite similar IV-results. The series resistance and the fill factor respectively seem to be dependent on the printing speed. The values for  $R_s$  are slightly increased with an increased printing speed. Especially the line conductivity and the contact resistance to the emitter, contributing to  $R_s$  during contact formation. The printed contact height decreases with printing speed from 5-6  $\mu\text{m}$  (5 mm/s) to about 2  $\mu\text{m}$  (25 mm/s). After firing in an inline belt furnace, the seed layer printed at 25 mm/s has no measureable line conductivity, whereas for the contact fingers printed at 5 mm/s sufficient material is deposited and a conductive finger could be formed. However the conductivity of the seed layer can be neglected, as the line conductivity is determined by the amount of plated silver. As all cells are plated under the same conditions in an LIP bath, the content of plated silver is similar for all cells and the measured line conductivity, is in the same range of (3.0 - 3.5×10<sup>-8</sup>  $\Omega\text{m}$ ). The relation between FF and printing speed can still be a result of an improved contact resistance. However, similar contact resistances for all cells, printed at different speeds could be found. The contact resistance for the cell printed at 25 mm/s was determined by TLM to  $R_c \times W=0.5 \Omega\text{cm}$ . The influence of printing speed on  $R_s$  is probably based on a combination of an improved series resistance and contact resistance.

**Table 1:** IV-results for 15.6×15.6 cm<sup>2</sup> mc-solar cells,

$v_{\text{print}}$ [mm/s]	$A$ [cm <sup>2</sup> ]	$V_{oc}$ [mV]	$J_{sc}$ [mA/cm <sup>2</sup> ]	$FF$ [%]	$\eta$ [%]	$R_{s, \text{light}}$ [ $\Omega\text{cm}^2$ ]
5	243.4	610	33.9	78	16.1	0.79
10	243.4	610	33.8	77	15.9	0.96
20	243.4	611	34.1	76.6	16.0	1.06
25	243.4	611	34.2	76.8	16.0	0.99

## Conclusion

Metal aerosol jet printing is demonstrated to be a reliable technique to create a seed layer for front side contacts on silicon solar cells. With hotmelt ink, developed for aerosol jet printing, the heating of the substrate is not necessary and excellent contact geometries can be achieved (see Figs. 6 and 7) at room

temperature. The aerosol printing system is adapted for hotmelt inks and large-area multi-crystalline solar cells were produced, achieving efficiencies as high as 16.1%.

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