ELECTRICAL PROPERTIES OF AEROSOL PRINTED CONTACTS

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ABSTRACT: The influence of printing height of the seed layer on the front side metallization was investigated. Therefore, solar cells were metalized using the aerosol printing technique and the seed layer ink for the metallization of solar cells (SISC) developed at Fraunhofer ISE. The single lines were deposited one over each other increasing the amount of ink per contact area. After contact firing and light-induced plating, the contact resistance was determined using the transfer-length model (TLM). The finger geometry was determined from cross sectional measurements and the conductivity from 4-probe measurements. In order to analyse the relationship between the amount of printed ink and the contact quality, the metal contacts were removed in an HNO_3/HF etching step and the metal semiconductor interface was analyzed via SEM images. It could be shown that a very thin single-printed seed layer leads to the best contact properties.

Keywords: Silicon solar cell, aerosol printing, light induced plating, silver crystallites, contact formation, contact geometry, line conductivity

1 INTRODUCTION

Actually, screen printing is the most commonly used metallization technique to fabricate front-side contacts on silicon solar cells. Due to the limitations of this technology it is important to find better techniques to metalize a silicon solar cell. Therefore several printing techniques were investigated over the last few years at Fraunhofer ISE [1]. One of these printing technologies is aerosol jet printing [2]. As it is a contact-free technology, aerosol printing can handle very thin substrates without stressing them mechanically resulting in a much lower breakage rate. Beside that, the aerosol jet stream can be focused and deposited as a seed layer with a line width below 20µm depending on the nozzle, substrate surface texturing and ink rheology. The aerosol-print technology is mainly used to deposit a metal seed layer which is thickened in a further metallization step called light-induced plating (LIP) [3]. In this work we studied the influence of the ink density on the electrical contact properties like line conductivity and contact resistance. The term 2-layer-metallization process used throughout this paper, means that the metal contact consists of a printed seed layer and a subsequent plated layer. The question of how thin a seed layer can be deposited to still achieve a good contact resistance and how much material is needed for a good electrical conductivity was investigated. For all experiments a seed layer ink (SISC) [4], developed at Fraunhofer ISE was used.

2 EXPERIMENTAL

The aerosol system was used to deposit contact structures of different heights by multiple layer printing (1 to 20 layers, one over each other). It is essential for calculating the specific line conductivity to determine the geometrical properties, especially the cross sectional area. We used a polished wafer to deposit the metal lines. The cross sections were determined by confocal microscopic measurements and verified with microscopic pictures from polished contact cross sections, see Figure 1. Finally the line conductivity was measured using a 4-probe measurement before and after plating.
In further experiments the relation between contact resistance and ink density [g/m²] was studied. The ink density quantifies the amount of solid ink ingredients (without solvents) per contact area. So, contact structures were printed with different velocities and heights (different ink densities) and were deposited on random textured Cz-wafers. The height of the lines changed between <1 µm to about 9 µm. After printing, the cells were fired in an industrial in-line furnace and subsequently plated by LIP. The contact resistance of each contact structure was determined by a TLM-measurement. A strong influence of the ink density on the contact resistance was found and could be explained by taking SEM images of the metal-semiconductor interface.

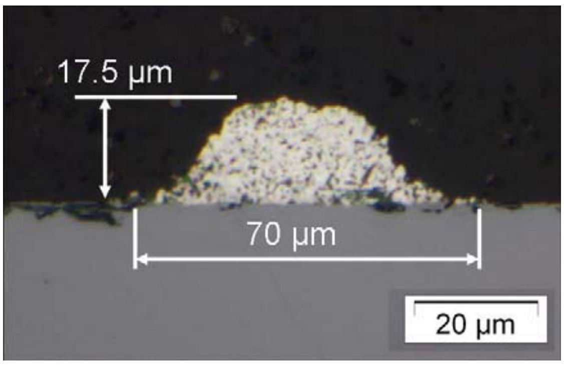

Figure 1: Cross sectional microscopic picture of a 20-fold aerosol printed “seed” layer.

3 CONTACT FORMATION

Figure 2 shows the schematic assembly of an aerosol printing head. The aerosol produced in an atomizer is lead to the printing head, where it next flows through the nozzle. In the printing head itself, there is second gas added to the printing system which encloses the aerosol stream like a sheath. Following the nozzle both aerosol and sheath gas exit the nozzle. By that, the sheath gas focuses the aerosol resulting in printed line widths which are significantly smaller than the inner diameter of the nozzle. The aerosol usually dries out on the hot printing chuck. The aerosol ink is deposited and the first step of the 2-layer-metallization is finished. Because of this technique and a hot printing chuck, there is no need to dry the ink in a further step.

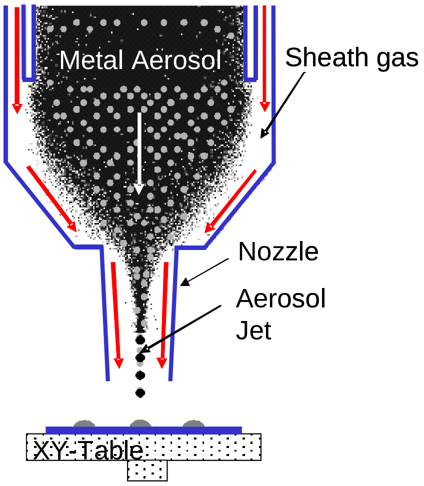

Figure 2: Scheme of an aerosol print head

In Figure 3 microscopic pictures of deposited seed layers after a single and a 20-layers print can be seen. It is obvious, that the 20-layer print is by far higher than the single layer print. On the first glance the aspect ratio seems to increase linearly.

a)

b)

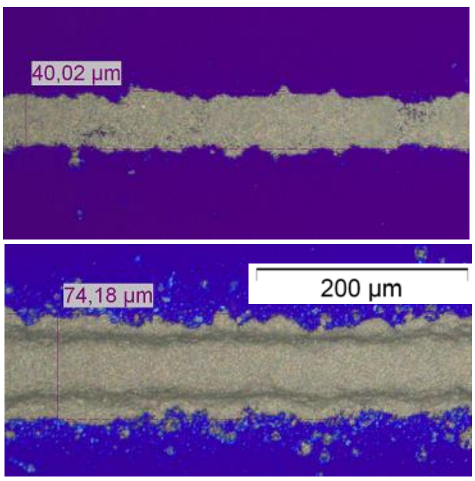

Figure 3: microscopic pictures of
a) 1-layer printed finger, and
b) 20-layer printed finger

4 CONTACT GEOMETRY

To determine the actual contact geometries, the printed fingers were measured with an optical confocal microscope. The graph in Figure 4 shows measured and averaged cross sections of multiple aerosol printed fingers. Additionally the cross section is determined from microscopic images of polished samples, see Figure 1. The cross sectional area is increased in width and height. With each deposited layer, the contact grew in height by about 1 µm. Fingers printed with 20 layers have a finger width of around 70 µm and a height of about 17 µm. Figure 4 underlines the first estimation resulting from Figure 3. Just out of this measurement one can say that the fingers heights are rising quite proportional to the amount of layers printed, unlike the finger widths. Thus, the aspect ratio, which is the ratio of contact height to contact width, is constantly growing, see Figure 5. After contact firing the aspect ratio is slightly reduced as the contacts mainly shrinks in height. This is due to the combustion of organic and the sintering of silver particles. This leads to the finding, that the line conductivities should correlate with the amount of deposited ink and therefore all printed fingers were measured before and right after the plating step (see chapter 5).

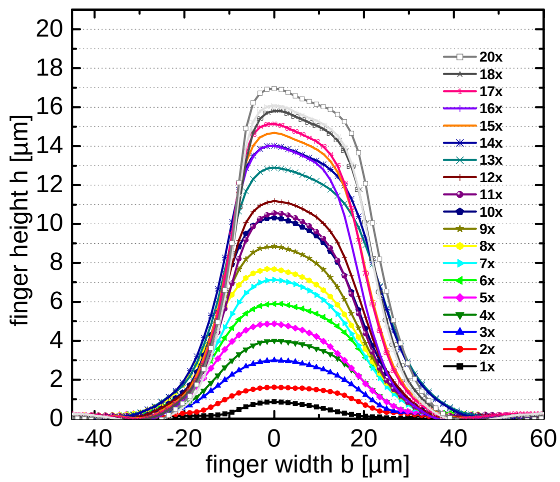

Figure 4: Cross section measurements from 1- to 20-layers (multiple; one over each other) printed fingers after the contacts have been fired.

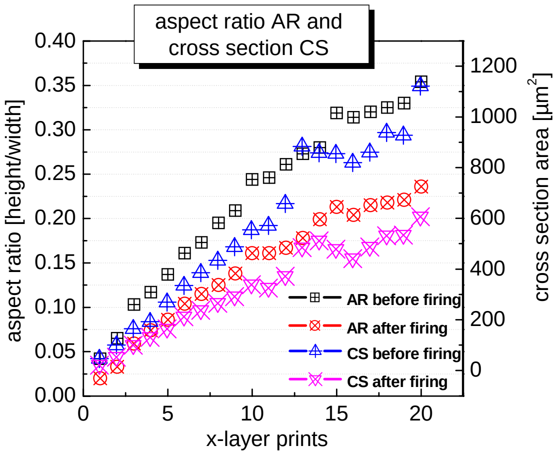

Figure 5: Aspect ratio (AR) and cross section measurements (CS) of multiple printed contacts. The aspect ratio is rising. This means that the multi-layer printed contacts are growing more in height, than in width.

5 LINE CONDUCTIVITY

Structures for measuring the line conductivity were printed. The relationship between the amount of the deposited ink and its conductivity is shown in Figure 6 Considering the conductivity before plating, it is rising constantly with the amount of the printed layers. After plating, the conductivities behave the other way around. That means the thinner the seed layer and thicker the plated silver on it, the better is the final conductivity of the whole line.

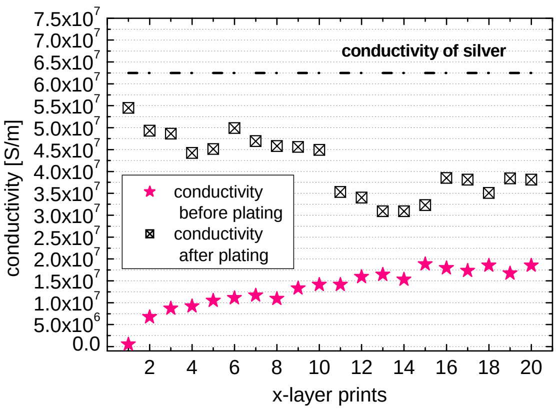

Figure 6 shows the line conductivities after firing and after plating. The dashed line marks the conductivity of bulk silver.

Although, the conductivity before plating is rising with the amount of layers printed, it would not be possible or at least very difficult to achieve the conductivity of plated silver, just by printing more layers. From a printed contact height of h_c=15 µm the conductivity saturates at a level of 2.0×10^{-7} S/m. Higher values are not possible with the used SISC ink, as it was developed for effective contact formation and not for a high line conductivity. Even with the 20-layer printed finger we didn't achieve half of the conductivity of the plated 1-layer finger. It is obviously much better to print the seed layer as flat as possible and to plate the rest of the finger with silver. With such a thin seed layer printed an plated contact structure, line conductivities, close to the value of bulk silver could be achieved.

6 CONTACT RESISTANCE

The determined contact resistance is strongly dependent on the ink density. The more ink per contact area is present; the higher is the measured resistance (see Figure 7).

The measured emitter sheet resistance (R_{sh}) is a proof for the quality of the measurement. The measured sheet resistance for every test structure is around 48+/-5 Ω/sq., which is consistent with the expected R_{sh}. Additionally, the heights of the fingers, according to the ink density, are plotted.

Different amounts of ink were deposited by printing again multiple layers. These contacts were measured after contact firing and light-induced plating, using TLM. The lowest values for the normalized contact resistance R_c*W [5] of 0.3 Ω cm were measured on a contact with a seed layer height below 2 µm. In this case an ink density of only 5 g/m² which is equal to an amount of 6 mg per wafer is sufficient to contact a large area solar cell (15.6 cm x 15.6 cm – 80 fingers, 2 busbars). The contact resistance is increased for higher ink densities or contact heights up to a value of R_c=0.8 Ω cm.

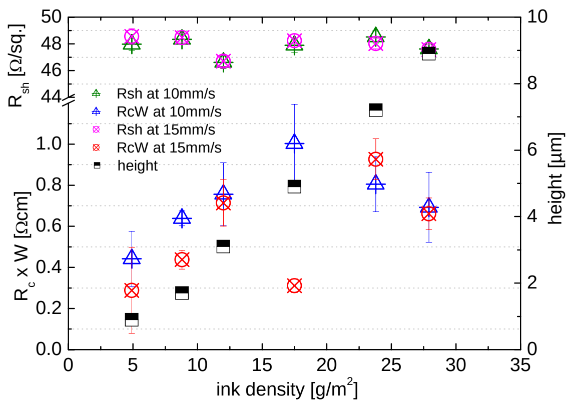

Figure 7: The contact resistance R_c x W rises up to an ink density around 15-20g/m². After that R_c x W decreases.

To get a better understanding of the relation between contact resistance and ink density, the contact silver was etched off and SEM-images of the metal-semiconductor interface were taken. Surprisingly, a constant amount of silver crystallites, which is mainly responsible for a high quality contact, could be found (see Figure 8a, b, c). At the same time an increasing opening of the SiN_x-passivation layer was observed. The higher the ink density the more SiN_x is "etched off" and dissolved in the glass layer, increasing the glass layer thickness even more.. A higher ink density is equivalent to a higher amount per contact area of reactive ink components (e.g.

glass frit). It is expected that there would be a better contact, if there is more SiN_x etched away, but when the ink density rises, the glass frit layer in the ink gets constantly thicker and starts to insulate more and more. Thus, the thinner the contact line (ink density) is, thinner is the glass layer and the better is the contact resistance.

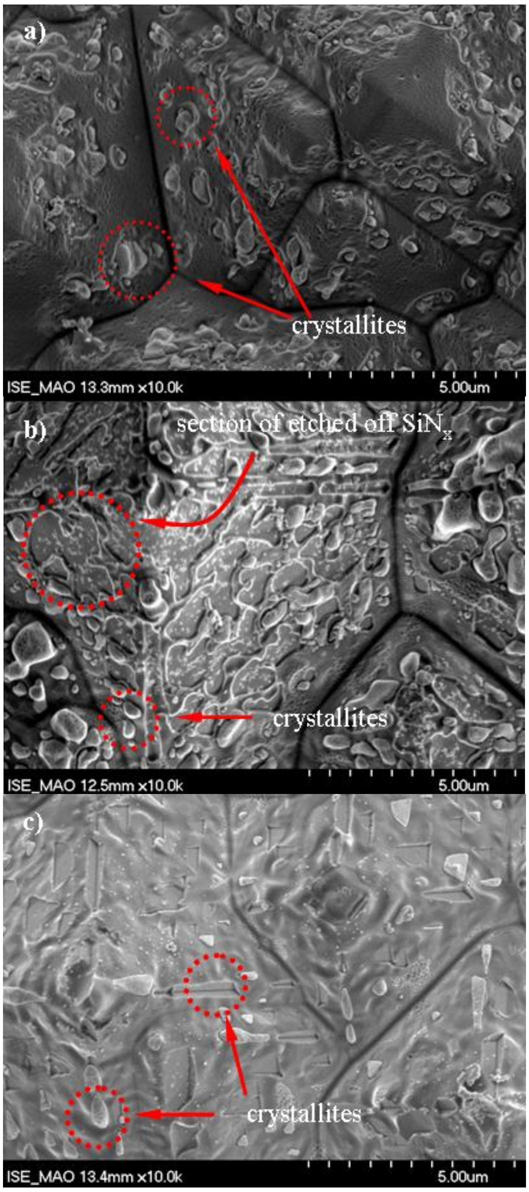

Figure 8: The front side metallization was printed and afterwards etched off with HNO_3 and HF. Therefore we got an image only of the silver crystallites and the cell surface.

a) Single printed contact with v = 20 mm/s (low ink density). A high crystallite density is visible. The SiN_x coating is locally opened.
b) Medium ink density, the crystallite density is approximately the same, but the SiN_x coating is strongly etched.
c) High ink density, the surface and the whole SiN_x-coating is etched away, but the number of silver crystallites or imprints is still constant.

For a good front side metallization a seed layer with an ink density as low as possible, but still enough to build up a high crystallite density, is needed.
It was proven, that the more ink is printed (and therefore the ink density is raising) the more the surface is going to be etched. However, this doesn't mean that the electrical properties are also getting better! It is shown in Figure 8c) how the amount of glass frit in the ink must have constrained the seed layer silver to build up silver contacts (crystallites) to the substrate. There are not more crystallites or imprints of crystallites compared to Figure 8a). So, it is no solution to print as much ink as possible, when at the end a "thick" printed finger gives not the guarantee to have a better electrical contact.

7 SUMMARY

The experiments showed that there is no problem to process a multi-layer deposition with the aerosol printer. It was proven that a certain combination of our processes at ISE rises up the quality of the front side metallization. The deposition of SISC ink should be as little as possible to create a very thin seed layer with good contact characteristics. Instead of one "big" printed finger, with a increased contact- and line resistance it is beneficial to print one thin seed layer which is subsequently enhanced in a further plating step. In order to fabricate a good low/ohmic contact it is important to design and use an optimized ink (→efficient glass frit, enough sliver particles and at the same time good printability. In this paper we observed a correlation between the contact resistance and the amount of ink. It could be shown that a thin single-printed seed layer followed by an effective plating step leads to a lower contact resistance and a greater line conductivity than a conventional printed finger and therefore a good perspective in the future.

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