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Investigations of Thick-Film-Paste Rheology for Dispensing Applications

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Abstract

In order to establish dispensing as a promising metallization process in silicon photovoltaics, equipment and metal pastes require further optimization. By conducting several rheological experiments based on rotational tests, shear thinning as well as thixotropic behavior of thick-film pastes were investigated. Both are crucial parameters for continuous dispensing of 60 µm fingers with high aspect ratios. Flow rate fluctuations during dispensing though imply stress peaks that may disturb a continuous paste flow. Thus, a comparison of the flow rate of two pastes was conducted. A comparison of dispensed cells with screen-printed reference cells, on multi-crystalline wafer-material, showed an efficiency increase of 0.3%abs. on average. This is mainly caused by reduced finger widths and higher aspect ratios of dispensed fingers.

Keywords: thick-film-paste; rheology; dispensing; metallization; printing;

1. Motivation

Thick-film metallization is an established production step in the crystalline silicon photovoltaic industry, forming robust contacts with proven long term stability. Dispensing of silver pastes as introduced by Chen et al. [1] combines the advantages of long term experience with thick-film pastes, with those of a non-impact approach, thus allowing high aspect ratios.

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However, substantial differences in operating conditions between screen-printing and dispensing also require further optimization of both, dispensing setup and printing medium.

Various other solutions were presented concerning dispenser setup [2-4] and grid layout [5]. Specht et al. [6] demonstrated average cell efficiency gains of 0.2%abs. and 0.3%abs. on multicrystalline and Czochralski material respectively. The same metal paste was used for screen-printing and dispensing. Furthermore, an optimization of paste rheology towards the dispensing process should increase process stability and cell performance.

2. Approach

2.1. Paste rheology depending on shear rate

Thick-film pastes used for metallization contain a high solid fraction of small silver particles and glass frit, surrounded by liquid binders and solvents (i.e. paste vehicle). Important characteristics of such systems are described by rheological terms, containing elements of both, rigid body and fluid dynamics.

During the printing process, the paste changes its properties from solid to liquid depending on applied conditions. Especially remarkable is shear thinning as well as thixotropic behaviour. Shear stress τ , responsible for friction losses in Newtonian fluids is caused by a tangential velocity gradient called shear rate $\dot{\gamma}$ (Fig. 1) and further depends on the viscosity η of the moving fluid (1) [7]:

$$\tau = \eta \cdot \dot{\gamma} = \eta \cdot \frac{dv}{dy} \tag{1}$$

Unlike Newtonian fluids, metal pastes reduce their viscosity $\eta(\dot{\gamma})$ with increasing shear rate $\dot{\gamma}$ due to a changing orientation of long chain molecules [7] in the paste vehicle. This behavior can be approximated using Ostwald-de Waele's Power-Law for shear rate $\dot{\gamma}$ (2) and shear stress τ (3):

$$\eta(\dot{\gamma}) = c \cdot \dot{\gamma}^{p-1} \tag{2}$$

$$\tau(\dot{\gamma}) = c \cdot \dot{\gamma}^{p} \tag{3}$$

The consistency *c* indicates the viscosity at an applied shear rate of $\dot{\gamma} = 1s^{-1}$. A power-law index $p < 1$ indicates shear thinning behaviour, $p > 1$ is valid for shear thickening materials (e.g. sand) and $p = 1$ resembles an ideal viscous Newtonian fluid with shear independent constant viscosity η [7].

This correlation can be confirmed by performing a rotational test for the desired pastes. For the investigations in this work, a rotational rheometer, type Physica MCR101 equipped with a 25 mm cone was used. Increasing the shear rate in a range of $\dot{\gamma} \in [10^{-2};10^{3}]s^{-1}$, led to the expected viscosity characteristic (Fig. 2).

Paste 1 and 4 are specially adapted dispensing pastes and thus more viscous than both screen printing pastes (P2 and P3). Furthermore, paste 2 shows a typical structural resolving process of long chain molecules [7] in the paste vehicle, visible as saddle point in the region around $\dot{\gamma} \approx 2s^{-1}$.

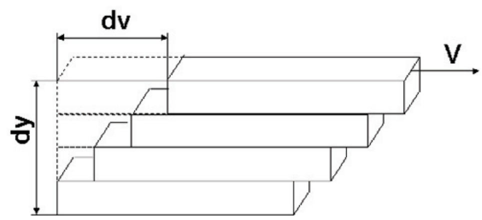

Fig. 1. Velocity distribution in laminar flow, induced by wall friction.

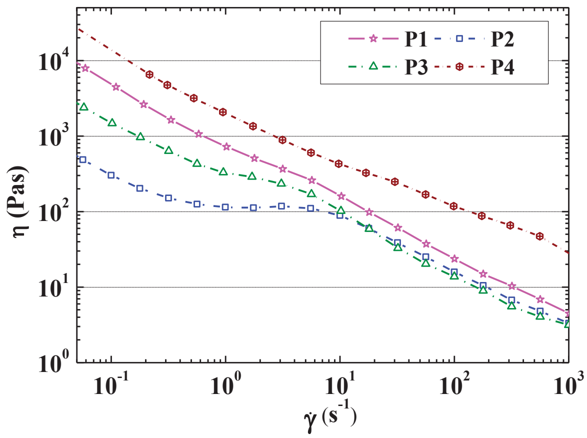

Fig. 2. Rotational test: Viscosity vs. shear rate with various metal pastes (P1 - P4).

2.2. Thixotropic effects

Thixotropy resembles a time-dependent change in viscosity due to structural changes in the medium, implied by a sudden load change. It is of major importance for most printing processes and can be measured in a 3 interval time test (3ITT) using the same rheometer [7]. In the first interval ($t_0 < t < t_1$), a low shear rate $\dot{\gamma} = 0.25 s^{-1}$ is applied to determine initial conditions. The short load phase ($t_1 < t < t_2$) implies a high shear rate $\dot{\gamma} = 5000 s^{-1}$ to the paste simulating the actual dispensing step – the paste is transferred through a very small nozzle of just around 100 µm in diameter.

This load impulse significantly reduces the viscosity, as the structure of the paste is destroyed. Thus, pressure losses in the dispensing nozzle are significantly reduced ensuring printability of the paste. In the last step ($t_2 < t < t_3$), a sudden drop of the shear rate back to its initial value induces the relaxation process and thus a time response of the viscosity (Fig. 3). Thixotropy indicates the paste relaxation in the first couple of milliseconds after the printing process, which are relevant for the spreading behaviour of the paste on the wafer, as demonstrated by Neidert et al. [8].

Unfortunately, high shear rates as applied in this investigation require a very high rotation speed of the rheometer. Thus, resulting measurements are strongly influenced by the inertias of power train and measuring cone. Consequently, not only shear rate $\dot{\gamma}(t)$ and viscosity $\eta(t)$, but also a direct correlation between the two should be analyzed. By plotting a time variant consistency *c(t)*, the time response of the paste is visible regardless of inertia effects (Fig. 3).

During the dispensing step ($t_1 < t < t_2$), an increased consistency *c(t)* indicates an incomplete restructuring process of the medium. Therefore, the viscosity is higher during this short load peak (i.e. dispensing viscosity) than assumed by using the power law equation (2). In fact, plotting these data next to the power law curve (Fig. 4), leads to a parallel movement during the dispensing step. The paste recovery in the third phase ($t_2 < t < t_3$) is then in good accordance again to the original power law curve.

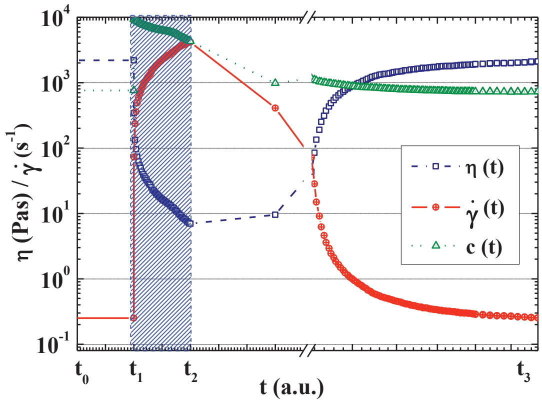

Fig. 3. Thixotropic impulse response of paste 1. The hatched area indicates the simulated dispensing step ($t_1 < t < t_2$).

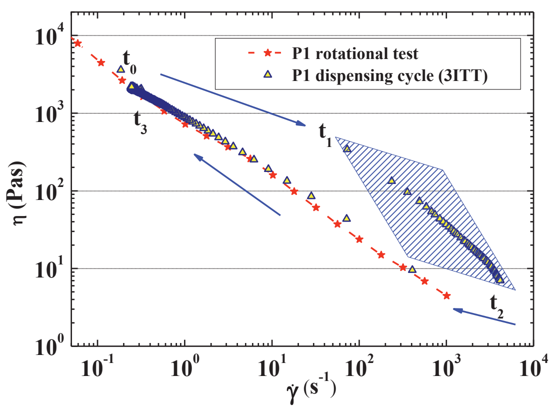

Fig. 4. Thixotropic impulse response depending on actual applied shear rate.

Not only the viscosity, but also the elasticity of the paste expressed by its shear modulus G influences the thixotropic behaviour of the paste. According to Hoornstra et al. [9], a high elasticity indicates a quick recovery process and thus little spreading on the wafer after the printing process.

As conventional printing methods still induce shear stress to the paste during snap off, an advantage of dispensing is its free flow phase, contributing significantly to the recovery process of the paste. Therefore, aspect ratios (height/width) reached through dispensing (AR~0.7) (Fig. 5), by far exceed those achieved by e.g. screen-printing (AR~0.13) [10].

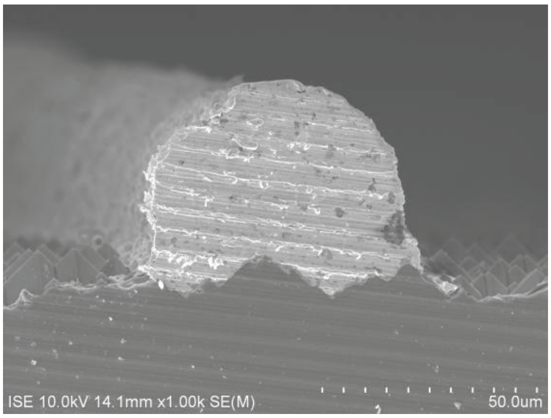

Fig. 5. Cross-section polish of dispensed finger on Cz material. Homogeneous dispensed width of 65 µm and height of 45 µm leading to aspect ratios of AR = 0.7 after fast firing process.

Having a certain cross section area optimized for good conductance, a higher finger reduces shading and reflective losses. Furthermore, decreasing the pitch as well as the cross section area per finger (thus increasing the number of fingers per cell) should lead to reduced electrical losses in the emitter region [10].

2.3. Flow measurements

Nevertheless, desired finger geometries with a width of 60 µm and below are quite challenging for both, dispenser and paste. Small fluctuations in the paste flow immediately lead to necking and stress peaks that may cause line interruptions. Therefore, extensive flow measurements had to prove stable printing of the time-pressure dispenser.

Throughout the experiments, different nozzles (length, diameter), pastes as well as the applied pressure were varied. Moreover, flow rates strongly depend on dispensing time due to thixotropic effects (Fig. 6). Optimized for dispensing applications, paste 1 stabilized throughout the experiment at constant medium flow rates. Its high fluctuation at the beginning of the experiment is most likely related to the influence of trapped air during the filling process of the cartridge. Applying similar conditions, paste 2, continuously increased its flow rate, reaching values twice as high as paste 1, which is in good accordance to its lower consistency as indicated earlier (Fig. 2). Both measurements show the importance of a controllable dispenser as well as a degasified dispensing medium.

3. Cell Results

In this work, a single nozzle dispenser was used in order to demonstrate the applicability of the pastes. The influence of various printing parameters on the solar cell results was tested on mc-Si 156x156 mm² precursor material equipped with soldering pads and standard aluminum printed back surfaces. As expected, dispensed fingers showed an increased cell performance, mainly due to their geometrical advantages leading to a higher charge carrier generation (TABLE I, Fig. 7).

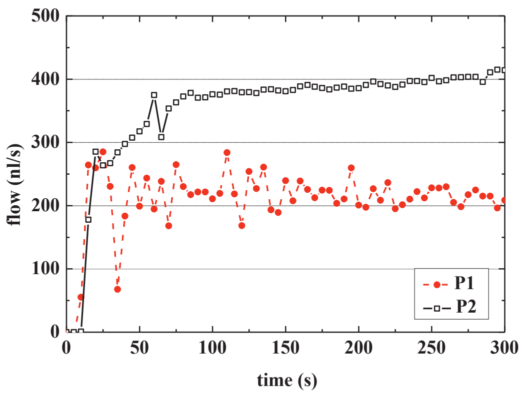

Fig. 6. Time-dependent flow rate in time-pressure dispensers.

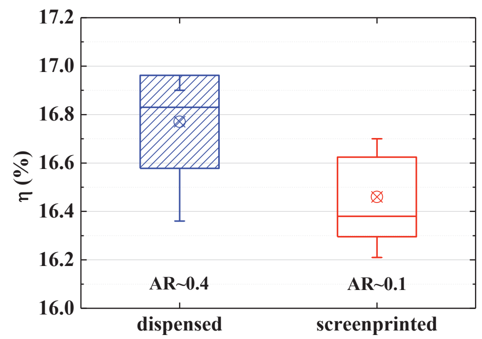

Fig. 7. Comparison of cell performances of respectively 10 screen-printed and dispensed samples on mc-material.

TABLE I. Average IV parameters of mc-cells.

Cell type	V_{oc} (mV)	J_{sc} (mA/cm^2)	*FF* (%)	η (%)
Dispensed	616.22	34.47	78.99	16.77
Screen-printed	615.97	33.80	79.11	16.47

Nevertheless, fluctuating results point out that process stability in dispensing still has to be improved. The number and position of finger interruptions has a significant impact on the series resistance R_s and thus on the fill factor FF [6]. Especially partially isolated fingers decrease the fill factor and therefore also the cell efficiency considerably.

In a different experiment on Cz- and mc-Si 156x156 mm² precursor material equipped with standard aluminum printed back surface, cell efficiencies of 17.3% on mc-Si and 18.4% on Cz-Si were achieved and approved by ISE CalLab.

4. Conclusion and outlook

In this paper, further aspects in correlation to dispensing as an alternative front side metallization process for silicon photovoltaics were discussed. By conducting several rheological experiments, shear thinning as well as thixotropic behaviour of metal pastes was investigated. High aspect ratio fingers of just 60 µm width were reached through dispensing.

Time fluctuation of the paste flow was found to be a critical parameter that has to be decreased in order to prevent stress peaks in the flow. These stress peaks may cause finger interruptions, possibly isolating finger sections from the busbars. A comparison of dispensed mc-cells with screen-printed reference cells, showed an efficiency increase of 0.3%abs. on average, mainly due to an increased charge carrier generation. Nevertheless, further optimization of paste rheology and dispensing setup is required, allowing to ramp up throughput rates, by subsequent parallelizing the dispensing process.

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