THE IMPORTANCE OF PASTE RHEOLOGY IN IMPROVING FINE LINE, THICK FILM SCREEN PRINTING OF FRONT SIDE METALLIZATION

Jaap Hoornstra, Arthur W. Weeber, Hugo H.C. de Moor, Wim C. Sinke
Netherlands Energy Research Foundation - ECN, PO Box 1, NL-1755 ZG Petten
P(+31)-224-564697, F(+31)-224-563214, hoornstra@ecn.nl

ABSTRACT: An important requirement in the processing of front side metallization for solar cells is to print fine lines with a high aspect ratio in mass production. Rheology is a key feature to describe the paste printing behaviour, but it is difficult to both characterize the aspects of easy printing and non-slumping using basic rotation viscometry. In this work a new approach is applied, using oscillation rheometry, to simulate the paste behaviour during printing in a single experiment. Time tests are performed on seven commercially available silver pastes, and are interpreted in terms of easy printing, slumping, etc. The results of screen printing tests on the seven pastes confirm the interpretation of the measured complex shear modulus and loss angle.
Keywords: Metallization - 1: Experimental methods - 2: Manufacturing and processing - 3

1. INTRODUCTION

Metallization is an efficiency limiting step in solar cell processing. For multi-crystalline solar cells an optimal front side metallization consists of multiple fine lines (fingers) and two wider connecting lines (busbars) arranged in an H-pattern. To diminish the effect of shadowing and yet to keep the line resistance low, the line width must be decreased and as a consequence the line height must be increased. On the basis of modelling it is found that the challenge is to obtain fingers of 50 μm width and 20 μm height after firing (meaning approximately 40 μm high after printing). In practice, however, there is a limitation in obtaining finer lines. Other mandatory features of the lines are good mechanical and electrical contact. In the laboratory fired dimensions of less than 100 μm wide and about 10 μm high are common. In the real world these figures cannot be met as concessions are made between high throughput and constant quality.

The dimensions and quality of the screen printed lines are determined by the screen definitions, the printing machine parameters, the paste characteristics and the cell surface characteristics. For solar cell processing much of the technology is inherited and adapted from the PCB industry [1]. The technological status of screen development and printing machine parameters are not limiting factors. For a dedicated printing machine operator it is feasible to combine the different, and generally contradictory, parameters and come to optimized results. The paste characteristics, however, are the least controlled by the user, and yet they have an enormous impact on not only the printing behaviour, quality and final line definition, but also on the fired film density and optimum contact of the particles with the silicon. A limiting factor is the availability of pastes with optimal printing characteristics. Up to now commercial solar pastes have been developed for their contacting and electrical behaviour, rather than to accommodate present printing requirements.
The aim of this study is to establish a connection between paste printing behaviour and paste rheology. The approach is to find a rheometrical procedure to simulate the behaviour of the paste during printing. Several commercially available silver pastes were subjected to screen printing and rheometrical tests and the printing characteristics are related to the rheometrical characteristics.
Next to this study, stencil printing, where also the paste rheology is important, is investigated [2, 3]. Here too, a goal is to improve the line definition.

2. PASTE CHARACTERISTICS

Solar silver paste is a suspension of functional particles in a solvent, to which a binder material is added. Silver particles show good conductivity and minor corrosive characteristics. The concentration of particles is about 70 to 80% on mass basis (being 25 to 30% on volume basis). The silver particles can be different in shape (spheres and flakes), size (1 to 5 μm) and size distribution. Generally particles are applied in the shape of flakes, but combinations are possible, and seem to improve the contact with the substrate. Glass frit is added in small quantities (up to 5 %) to enable good sintering and contacting behaviour during the formation of the contacts. On the other hand, the amount of glass and also the formulation must be taken with care, because glass also forms an insulating layer between the silver and the silicon substrate, and can result in etching through the emitter during the high temperature sintering process. In general, glass frit particle sizes are in the same order of magnitude as the silver particles, but sizes up to 15 mm are possible. Paste composition and characteristics can be different per type and also per manufacturer. Paste also contains small quantities of other organic additives to improve amongst others the lifetime. The rheological behaviour is dependent not only on the relative silver volume, the particle shape and size distribution, the organic vehicle and binder, but also on additives used to modify the rheology. After printing the paste is generally dried at about 125 to 250°C. The remaining organics are then further burned out in a firing step, where also the sintering of the silver particles takes place at temperatures ranging from 650 up to 850°C [4].

Paste printing behaviour is characterized by its rheology. For fine line, thick film printing it is important that the paste can be printed easily and produces the required fine and continuous lines with a high aspect ratio. This implies that it must be easy to squeegee the paste over the surface and through the small openings of the screen and deposit the paste on the silicon substrate. For this purpose the paste must exhibit a shear thinning, or pseudo-plastic, behaviour, meaning a reduction in viscosity or an increase in shear stress at increasing shear rate. After raising the screen the paste must completely release from the screen openings and regain its structure fast, so that it does not spread or slump. Slumping, a term used in PCB industry, will cause the printed line to lose height and gain width starting just after the screen is released. Depending on how fast the paste can regain its structure slumping can occur up to minutes after the release and can be stopped by proper use of the drying step [4]. Due to slumping the printed line width can be up to 1.5 times (or more) the line width in the screen. In the case of a screen some levelling of the paste is needed. Thixotropic behaviour, which is a time dependent change in viscosity, is related to the recovery of the paste.

As a rheological parameter the dynamic viscosity h at a certain shear rate g is commonly used. In some cases the slope of the curve, the pseudo-plastic index, is added. The index is a measure for the shear-thinning behaviour. These data are basically applied for quality control and assurance of the manufacturer [5], but are of limited practical use in case of fine line, thick film printing. For the investigated paste typical dynamic viscosity values range from 900 to 2000 Pa.s at a shear rate of 0.1 reciprocal seconds.
Simple shear experiments are not sufficient to completely characterize the paste. Since silver paste, being a particle suspension, also shows visco-elastic behaviour, dynamic measurements such as oscillation measurements can be performed to describe the viscous and elastic behaviour. The complex shear modulus G* is then measured, of which the real and imaginary parts, the storage G' and loss G'' moduli, represent the elastic and viscous behaviour. So far no literature on dynamic rheology measurements on solar silver paste was found.
Rheological changes in the paste during printing are time and shear dependent and specifically the actions during and just after the print stroke are framed in milli-seconds.

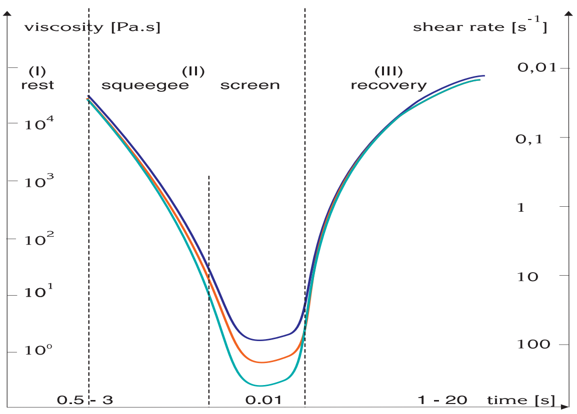

Figure 1: Evolution of viscosity and shear rate during printing

Figure 1 shows the evolution of viscosity and shear rate prior to, during and after printing using a screen. The figure, taken from [6], is adapted for our application, where the shear rate is calculated for a typical screen. Initially, when the paste is at rest, it shows a relatively high viscosity and low shear rate. If stirring is applied prior to printing, it will reduce the viscosity. Further reduction is caused by the squeegee action when the paste is rolled in front of the squeegee over the screen surface. The fastest change in viscosity and shear rate is caused by forcing the paste through the screen (mesh) or stencil openings.
Behind the squeegee, when the paste is pressed through the openings, the shear rate returns to original proportions and the viscosity increases as the paste recovers its structure. The speed of the increase will determine the recovery of the paste structure and is a measure for the slump. In case of using a snap-off the screen is lifted directly behind the squeegee. If no snap-off is used the paste has little more time to regain its structure but will be disturbed again by the lifting of the stencil.
In figure 1 three curves are given. The paste flow behaviour during the squeegee movement is not understood in detail and is dependent on different assumptions. Consequently the flow behaviour is difficult to model and the calculated shear rates show some uncertainty. During the action of filling the openings in the screen the shear rate will have its maximum value, and is supposed to range up to more then 1000 reciprocal seconds.
In practice, easy printing can be met using a relatively low viscosity paste, but non-slumping needs a contradictory quality. In general commercially available pastes can be printed fairly easily, but show extensive slumping actions, broadening the printed lines by over 50%. If, on the other hand, a paste is produced for less slumping, then it is extremely difficult or impossible to print and to keep the printing quality under control in mass production. This often leads to blockages in the screen (clogging) or interruptions in the printed lines.

3. MEASUREMENTS AND RESULTS

To monitor the different stages during the printing process measurements with different rheometers were performed. The viscous properties were measured using rotation viscometry and to identify the visco-elastic behaviour of the pastes oscillation rheometry was used. In addition to these measurements silver pastes were printed. Seven commercially available pastes were used in the testing.

As a first step to describe the printing behaviour flow curves (shear stress vs. shear rate) were measured and the viscosity curves were deduced. The measurements were performed using a Carri-Med CLS 50 instrument and the shear stress results for 4 typical pastes are presented in figure 2. The results show a shear thinning behaviour for all the pastes and distinctive variation in the flow curves, where paste 5 is a typical standard, low viscosity paste and paste 2 is a high viscosity paste used for stencil printing.

The thixotropic behaviour is represented by the hysteresis in the flow curves.

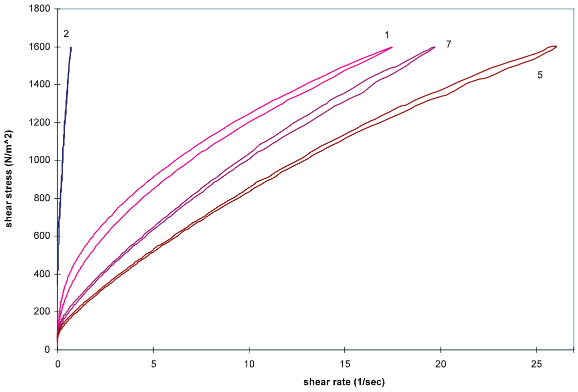

Figure 2: Shear stress as a function of shear rate for four typical pastes.

The viscosity measurements were compared with the print results. The seven silver pastes were screenprinted by standard methods under nominal conditions. It was not the aim of the printing to obtain optimal lines, but more to be able to compare the different pastes in their printing behaviour and results. After printing, the wafers were subjected to infrared drying at 125°C. The line width and line height of the dried fingers was measured using an optical microscope. In table 1 the printing results are summarized. From the line width and line height of the printed lines the aspect ratio was calculated. Since a few microns in height has an enormous impact on the aspect ratio, also the relative line width was calculated, being the ratio of the measured line width and the line width of the fingers in the screen.

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
A.R.	0.11	0.24	0.11	0.11	0.16	0.15	0.16
R.L.	1.41	1.15	1.39	1.50	1.36	1.30	1.38

A.R.= Aspect Ratio - line width/line height print after drying

R.L.= Relative Line width - line width print/line width screen

Table 1: Normalized printing results for seven pastes.

The printing tests confirm the measured flow curves in the general printing behaviour: the high viscosity paste 2 is difficult to print and paste 5 allows for easy printing.

It is, however, not possible in a flow test to subject the paste to the dynamic stages it experiences during printing. The slumping aspect therefore cannot be predicted from the data of the flow curves. An indication might be the thixotropy coefficient, but the speed at which the shear rate is changed during the measurement will influence the measured shear stress (or deduced viscosity) results and consequently the hysteresis between the up and down measurement of the flow curve as caused by thixotropy. Also the change in shear rates is rather different than the shear history during printing.

Further limitations of the viscosity measurements are that part of the printing action occurs at shear rates that surpass 100 reciprocal seconds and also the range of the instrument. Another aspect is that it is difficult to set the instrument parameters enabling comparison of all results: a high viscosity paste might need a different setting than a low viscosity paste, and also the paste under investigation needs to have the same history.

For the purpose of studying the slump behaviour, time dependent oscillation (or dynamic) tests using a Physica UDS-200 MK21instrument were performed.

An approach to simulate the paste behaviour during printing in the oscillation measurements is in a time test, where the paste is subjected to three intervals: I-pre-print, II-print and III-post-print. In the first interval, representing the period prior to the squeegee action, where the paste is at rest, a torque is applied with a frequency of 2 Hz and an amplitude of 100 mNm allowing for the paste not to deform its structure. In the next interval the torque is increased to 20 mNm to simulate the paste being moved by the squeegee and pushed through the openings of the screen. In the third interval the amplitude is then returned to its initial value and the paste can recover and regain its structure. During the time test the storage modulus G' and loss modulus G" are measured, representing the elastic and viscous behaviour of the paste.

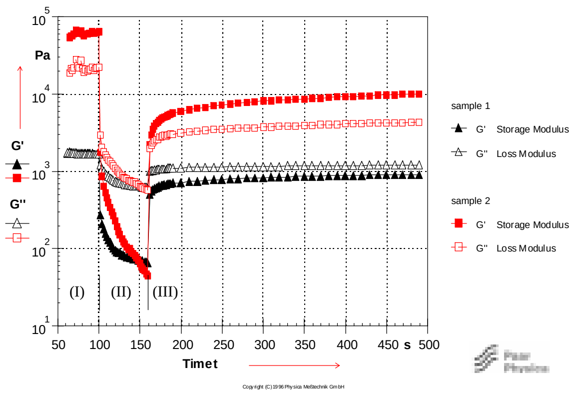

Figure 3: Example of measured loss and storage modulus for two pastes.

An example of the results is presented in figure 3, where a stencil paste 2 is compared to a screen paste 1. In the rest interval (I) paste 2 shows a more elastic (meaning solid) behaviour than paste 1. During the print interval (II) the elastic component drops dramatically under the viscous component for both pastes. The fact that paste 1 is easier to print is reflected by the lower value of the loss modulus just after the amplitude is increased but also in the rounded form of the curve. Directly after returning the amplitude to its original value the elastic component of paste 2 quickly exceeds the viscous component, showing a fast recovery of this paste and indicating less slump. The elastic component of the paste 1 is only slowly recovering.

Another way of looking at the data is to use the phase shift or loss angle δ, being arc tan G"/G'. If the viscous component G">> the elastic component G', and consequently δ→90°, the paste is easy to print. If, directly after the paste is released, G"≤G' and consequently δ ≤45° a fast relaxation behaviour after printing is shown. Further increase of the elastic component G' in time is better for a non slumping behaviour.

The loss angle for the seven pastes is given in figure 4. From the results it can be observed that paste 2 and 6 are more viscous in the pre-print interval (small δ). All pastes have basically good printing behaviour (δ » 90°) in interval II, although paste 2 is difficult to start. Paste 2 has least slump and gives narrow lines (fast recovery after printing to δ<45°). The smaller the value for the loss angle δ after relaxation indicates an improved aspect ratio. These figures are confirmed by the results of measurements of the line definition and relative line width after printing.

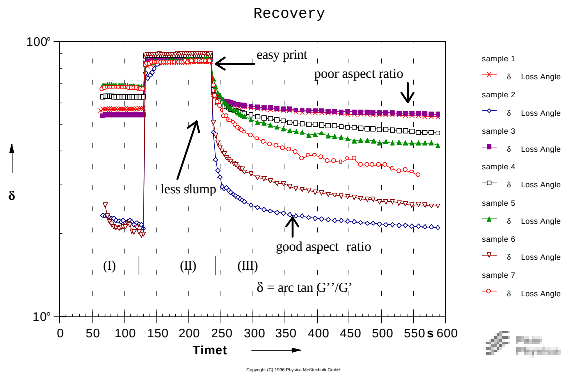

Figure 4: Loss angle for seven pastes.

4. CONCLUSIONS

In general, pastes are prepared for easy printing rather than for printing fine lines with a high aspect ratio. In practice these aspects are not accommodated together in the pastes. Rotation viscometry can be used as a first order predictor of print behaviour of the pastes, but does not duplicate the shear history of the paste during printing and cannot be used to indicate the slumping behaviour. The presented time sweep test in oscillation rheometry, where the complete print process is simulated, allows for identifying the easy printing character and the recovery action after printing in a single measurement. Screen print results of seven pastes confirm the outcome of the rheometrical oscillation time tests.

ACKNOWLEDGEMENTS

Klaus Wollny of Physica Messtechnik GmbH, Stuttgart, Germany, performed the rheometrical tests and supported the evaluation of data.

The work has been carried out within the framework of ECN's Long Term Energy Research Program ENGINE and the Joule III project "DOLMET" under contract number JOR3-CT95-0040.

REFERENCES

[1] Dziedzic, D., Nijs, J. and Szlufcik, J., "Thick-film Fine-line Fabrication Techniques - Application to Front Metallisation of Solar Cells", Hybrid Circuits, No. 30, January 1993.

[2] Moor, H.H.C. de, Weeber, A.W., Hoornstra, J. and Sinke, W.C., "Fine-line Screen Printing for Silicon Solar Cells", Snowmass Conference, Colorado,1996.

[3] Moor, H.H.C. de, Hoornstra, J., Weeber, A.W., Burgers A.R., and Sinke, W.C., "Printing High and Fine Metal Lines Using Stencils", 14th EPSEC, Barcelona, 1997.

[4] Kruzek, R. and Vogt, L., "Infrared Furnaces for Firing Solar Cell Contacts", RTC-publication, Anaheim, CA.

[5] Provance, J.D. and Allison, K., "Particle Size Effects on Viscosity of Silver Pastes - A Manufacturer's View", Int. J. for Hybrid Microelectronics, Vol. 6, No. 1, p.60, October 1983.

[6] Trease, R.E. and Dietz, R.L., "Paste Rheology Can Improve Your Fine Line Printing", Proceedings ISHM, p.8.4.2, 1970.