Particle Inks for Inkjet Printing of Electronic Components

Ulrike Currle, Marcel Wassmer, Klaus Krueger; Helmut-Schmidt-University/University of the Federal Armed Forces; Hamburg/Germany

Abstract

Digital printing of electronic circuits includes the deposition of a variety of particles, which determine the electronic properties after sintering. In general, the particles are non-colloidal which means that sedimentation occurs. In getting sedimentation under control, a wide range of particles can be printed.
In a first step, the sedimentation behavior of silver and glass particles is characterised in different organic solvents taking into account different sizes, shapes, densities and concentrations. The analysis of the sedimentation behavior is based on an optical method which allows for the detection of small concentration changes. In a second step, the particles are stabilised using commercial dispersants and the stability of the inks is evaluated. The influence of the particles on the viscosity is studied as well as the influence of the particles on the surface tension and wetting. Finally, chosen inks are printed on ceramic substrates by inkjet printing. After drying by evaporation and sintering, the shape and electrical properties of the electrical structures are analysed. The article discusses the design of functional particle inks, highlights properties and interactions and demonstrates the functionality of the designed inks by printing a capacitor.

Introduction

As inkjet printing of nano-silver inks becomes more reliable, its use for digital fabrication of microelectronic circuits gains in importance and it starts to cooperate or even to compete with thick-film screen printing [1,2]. For cooperation it is the first step to inkjet conductive lines but for competition further electronic components must be inkjet printable and compatible in processing. The electrical behavior is determined by the composition of metal, metal oxides and glass particles. Due to the high density of the metal particles and the limited miniaturization of glass particles, sedimentation occurs to be the major challenge for electrically functional inks. The stability of the ink is fundamental for stable drop formation. The viscosity must be suitable for the print heads' operational ranges and the inks' interaction with the substrate must be taken into account. Finally the processing of the ink must fit the requirements of the functional electrical circuits. In the following, the design of functional particle inks is discussed and for demonstration a capacitor is printed.

Sedimentation

Particles tend to settle down due to gravitational forces. In **figure 1** the settling behavior of 10 wt% glass powder (ρ=2.53 g/cm^3, d_{50}=1 µm) in terpineol ($\rho_{20°C}$=0.934 g/cm^3, $\eta_{20°C}$=61 mPas) is visualized.

For up to three hours, the ink seems to be stable. From six hours onwards a clear upper part and a sediment occur.

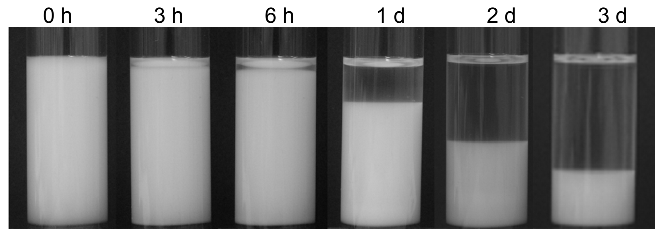

Figure 1. *Sedimentation of 10 wt% glass powder in terpineol*

The sedimentation process can be studied more precisely by vertical scanning of the sample and recording the transmission and backscattering signal with the Turbiscan Classic (Formulaction) as shown in **figure 2**. The transmission signal provides information about clearance effects while the backscattering signal detects concentration changes in the sediment. This method can also be applied to prove stability.

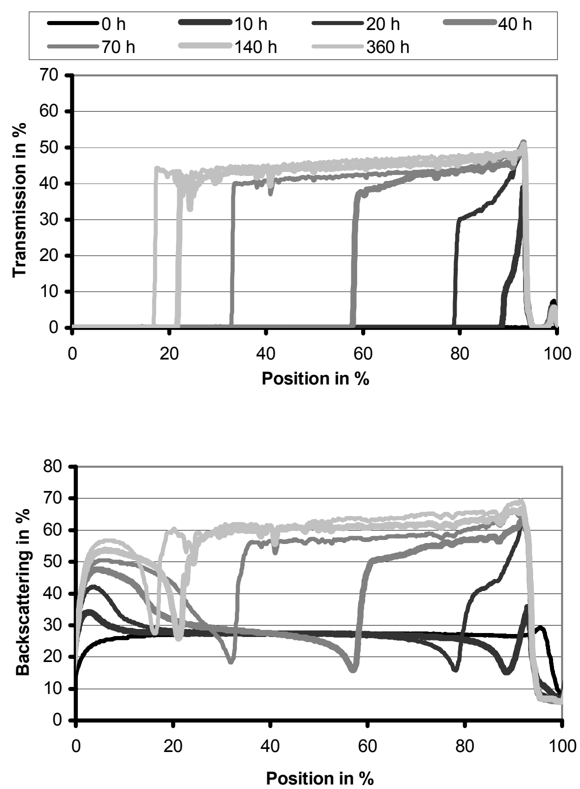

Figure 2. *Transmission and backscattering signal (10 wt% glass in terpineol)*

The transmission and the backscattering signal are clearly related to concentrational changes in the ink. **Figure 3** shows the relation between measured intensity and solid substance amount for the glass powder in terpineol. The relation is characteristic for each particle/fluid composition.

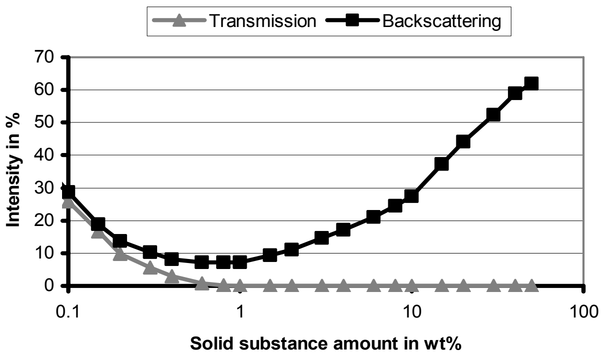

***Figure 3**. Relation between intensity and concentration for glass in terpineol*

Combining the measured signal in figure 2 and the relation in figure 3 allows for the calculation of a concentration profile which is given in **figure 4**.

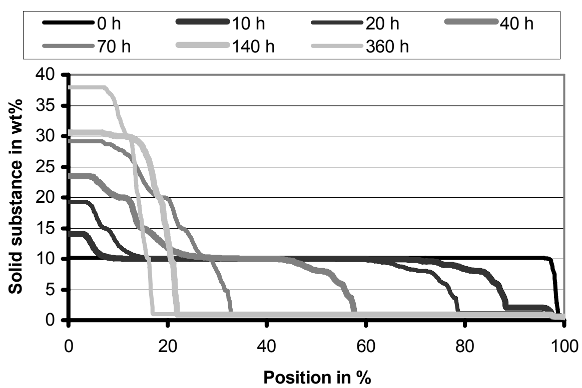

***Figure 4**. Concentration changes during storage*

The sedimenting ink exhibits three characteristic sections: Clearance at the top, constant (original) concentration in the middle and sediment at the bottom with increasing concentration. With slowly settling systems, the ink can be printed successfully from the "stable" part in the middle of the suspension [3]. As soon as the sediment is reached, satellite drops and nozzle clogging is likely.

The movement of the clear phase provides information about the sedimentation velocity of the suspension and allows for the comparison of different systems (**figure 5**). The movement of the particles can either be derived from the transmission signal in figure 2 or the concentration profile in figure 4.

Figure 5 shows some fundamentals about sedimentation: Quicker sedimentation, i.e. less stability is expected for

- low-viscosity fluids e.g. diethylene glycol monobutyl ether acetate (DGMBA) with $\eta_{20°C}$=2.4 mPas vs. terpineol (TER) with $\eta_{20°C}$=61 mPas,
- high density particles e.g. silver with ρ=10.5 g/cm^3 vs. glass with ρ=2.53 g/cm^3,
- large particles e.g. silver with d_{50}=0,3 µm vs. silver with d_{50}=0,08 µm and
- low concentrations e.g. glass at 10 wt% vs. 30 wt%.

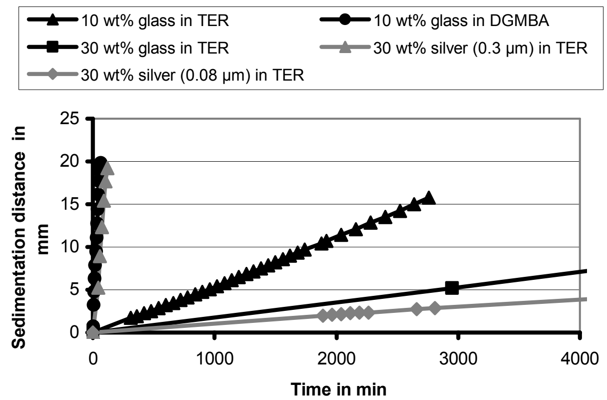

***Figure 5**. Sedimentation behavior*

By increasing the solid substance amount, a long term stable suspension can be obtained (**figure 6**). Unfortunately, the resulting suspension is not inkjet printable any more due to the high particle loading and the subsequent high viscosity. For stability reasons, it is helpful to increase the solid substance amount of an ink to the highest possible value that is still printable. Besides, a high particle loading reduces the fluid amount on the substrate.

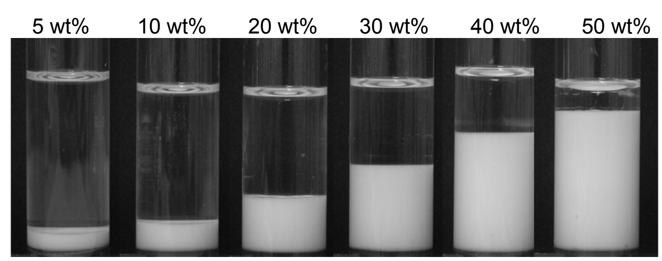

***Figure 6**. Long term stability of glass in terpineol (after 6 months)*

Particle Stabilization

Commercial stabilizing additives like Solsperse hyperdispersants (SP) and resins like cellulose ester (CE) help to increase the stability of particle loaded inks. Even small amounts of Solsperse hyperdispersants stabilize without influencing the viscosity of the solvent. Higher additive amounts do not significantly improve the stability, tend to clog the nozzle and might increase viscosity. In suspensions with a high particle loading, Solsperse hyperdispersants improve wetting and reduce the viscosity significantly. Resin shows a better long term stabilization effect than Solsperse hyperdispersants but increases the viscosity of the solvent. The stabilization effect of resin increases with its increases with its amount. The maximum possible resin amount is restricted by its solubility, the viscosity requirements of the print head and the probability of nozzle clogging. Resin is especially effective in combination with low-viscosity fluids. By combining both additives, the stabilizing effect of resin dominates. The stabilization effect of both additives bases on reducing the sedimentation velocity, i.e. the stabilization effect depends on the particle size, density and concentration (**figure 7**). The stabilizing effect can be influenced to some extent by the dispersion method [4]. By keeping the stabilized ink in motion e.g. by magnetic stirring or a circulating system, sedimentation can be delayed.

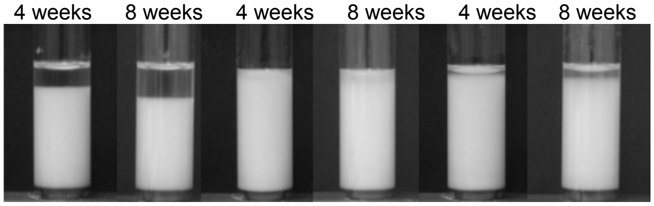

***Figure 7**. Stabilization effect of SP (amount in wt%, 10 wt% glass, terpineol)*

Ink Viscosity

So far it has been shown that a high viscosity of the fluid, a high resin amount and a high solid substance amount improve stability. However, the drop on demand process requires low viscosity inks with a printing viscosity of around 10 to 20 mPas, depending on the print head. One approach to achieve this key parameter is to combine a high-viscosity fluid with a stabilizing additive without impact on the viscosity or to add a small amount of resin and reduce the printing viscosity by nozzle heating. This approach requires a fluid with a high temperature dependence of the viscosity. Another approach is to use a low-viscosity fluid and add a high amount of resin to provide stability. In this case, nozzle heating might be avoided. The effect of the particles on the viscosity depends on their volume fraction whereas the viscosity behavior of an ink is mainly determined by the viscosity behavior of the underlying solvent-additive mixture [5]. Characteristic for most inks is the Newtonian behavior at printing viscosity.

Surface Tension

The surface tension of the ink influences the droplet formation. The sensitivity of the printing process towards surface tension changes depends on the print head. Measurements reveal that the surface tension of the particle ink is determined by the surface tension of the underlying solvent or solvent composition respectively.

Table 1: Suface tension σ of some particle inks

Solvent/Ink	σ in mN/m	stdev in mN/m
TER (terpineol)	30.9	0.2
TER + SP (Solsperse)	30.6	0.4
TER + SP + 30 wt% silver	30.2	0.9
TER + SP + 30 wt% glass	30.5	0.2
EG (ethylene glycol)	46.1	0.5
EG + SP + 30 wt% silver	45.5	0.6

Neither the stabilizing additives nor the particles nor the concentration of the particles seem to influence the surface tension. The variations in **table 1** are within the measurement tolerance which is about 1 mN/m (pendant drop method, DSA100, Kruess). As there are only additives for decreasing the surface tension available, the only remaining way for increasing the surface tension is mixing with a solvent with a higher surface tension. The surface tension changes in a linear way depending on the relation of the solvents while the viscosity may increase non-linearly from lower to higher viscosities.

Wetting and Interaction with Substrates

The printing result is influenced by the interaction between ink and substrate. In electronics, there is a variety of substrates of interest. In the following, a substrate with a high surface energy (Al_2O_3) and a substrate with a low surface energy (LSE) are considered. The contact angle between ink droplet and substrate describes the wetting behavior of an ink on a certain substrate. A contact angle measurement smaller than 5° (range limit, DSA100, Kruess) in **table 2** indicates total wetting. The droplet diameter provides information about the total spreading of the droplet on the substrate. Besides many other factors, the wetting behavior depends on the surface energy of the substrates, the surface tension of the inks, the selected additives and the particles themselves and is therefore hardly predictable. The spreading of the ink complicates fine line printing and miniaturization in the course. Spreading depends on the drying behavior of the ink, which is itself dependent on the choice of the solvents, the additives and the solid substance amount.

Table 2: Contact angle (*CA*) and diameter (*d*) on substrates

Solvent/Ink	*CA* in ° (Al_2O_3)	*d* in mm (Al_2O_3)	*CA* in ° (LSE)	*d* in mm (LSE)
TER	<5	18	<5	8
EG	29	3.5	83	2
TER + SP	<5	16	<5	6.5
EG + SP	16	5	74	2.5
TER + CE	<5	10	<5	8
TER + SP + Ag	<5	14	19	4
TER + CE + Ag	10	5	17	4
EG + SP + Ag	16	4	94	2.5

The ink composition influences the printing result as shown in **figure 8**. All inks are printed in the same way under the same conditions on the same substrate. While the different additives in terpineol only influence the shape and line width, the solvent butyl glycol (BUG) appears to be incompatible with the substrate. For an optimal printing result, the ink and the substrate need to be adapted to each other.

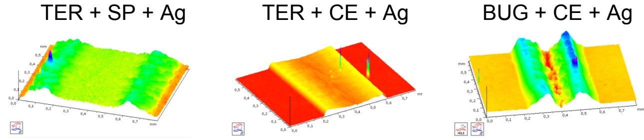

***Figure 8**. Influence of the ink composition on the printing result*

Besides the composition of the ink, there are several printing options to influence the printing result. To name only some the droplet size, the printing scheme, e.g. the distance between overlapping droplets, and the drying conditions show a significant effect. However, the optimal printing scheme is again ink dependent.

Printing Samples

In the following a 40 wt% silver ink (d_{50}=0.7 µm) and a 23 wt% glass ink (d_{50}=0.9 µm) are jetted on ceramic substrates. The printer consists of a stationary piezo-driven print head [6], an x-y-planar motor to position the substrate and an integrated heating plate to heat the substrate to up to 120 °C. No sedimentation occurred in the inks during the experimental period of about two weeks. For demonstration of a suitable ink formulation, a capacitor is printed.

First step is the printing of silver conductive lines as well as the terminations and the first layer of the plate capacitor. For conductive lines, on the one hand, a small droplet size is required to reduce spreading on the substrate and to realize narrow lines; on the other hand, a high layer thickness is needed to reduce sheet resistivity. Terminations and plate ask for sharp edges achieved by small droplet volumes; whereas fast production is achieved by large droplet volumes. The shape of the lines is also significantly influenced by the substrate and its temperature. A droplet volume of 200 pL allows for a width of 150 µm on ceramic substrates at 80 °C surface temperature. A printed line is shown in **figure 9**.

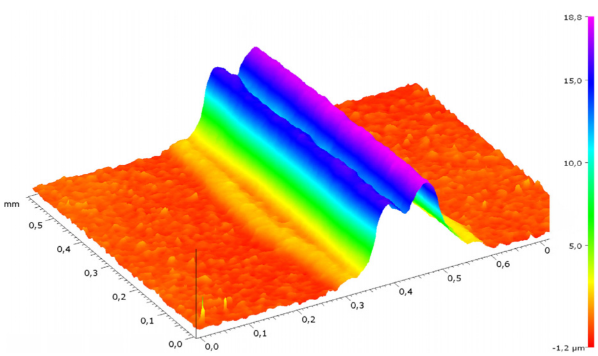

***Figure 9**. Inkjet printed silver line*

With a height of 17 µm, the sheet resistivity is 3.2 mΩ/sq. The conductance of the inkjetted silver is $18{\cdot}10^{6}$ S/m which is approximately 30% of the conductance of bulk silver. Increasing spot distance and decreasing droplet volume allow for even smaller dimensions but also result in much lower conductance. Because of the large dimensions of the terminations and the plates, a height of 10 µm or less is sufficient to achieve the required electrical properties. After drying and firing at 900 °C, in the next step the insulating dielectric layer is printed with the glass ink. The intended electrical property is a highly insulating layer of a homogenous height. As an overlap of the glass over the plate is needed, the ink has to cover two different levels in height and material. This influences the drying conditions as well as the ink and particle movement and it may result in an inhomogeneous glass matrix or even in potholes and therefore in connections between the plates. This risk can be minimized by reducing the droplet volume and by droplet volume and by increasing the overlapping area.

In the third step, the second capacitor plate and its connection to the conductive lines is printed. Because of the interfacial tension of the silver ink on glass matrix, much sharper edges occur compared to the first layer printed on the ceramic substrate. A critical section is the connection to the first layer. Since the conductive line has to step over the edge of the glass matrix, large cracks may occur due to different wetting behaviors, different coefficients of thermal expansion and shrinkage during firing. Adapting the shape of the glass matrix at the connection's side can reduce the tensions and therefore the cracks. Finally the third layer is fired. **Figure 10** shows the final circuit. The specific capacity of the capacitor amounts to 300 pF/cm^2.

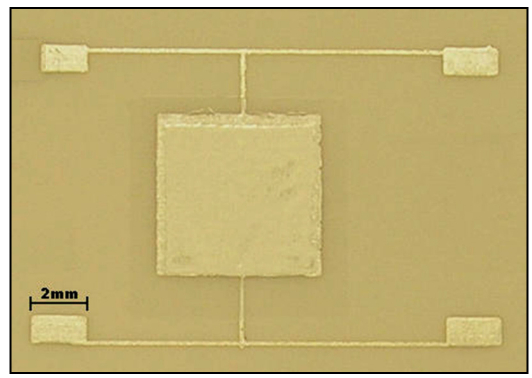

***Figure 10**. Inkjet printed conductive lines and capacitor*

Using the inkjetted capacitor a RC-circuit is built up. The electrical properties of the RC-circuit are investigated regarding its behavior as a low-pass filter. The very low capacity of the capacitor (60 pF) demands a measuring setup with very low capacities within wiring, probe and scope. The investigated low-pass filter has a theoretical time constant of $\tau_{th} = R{\cdot}C = 100$ ns. At first the system's step response is investigated.

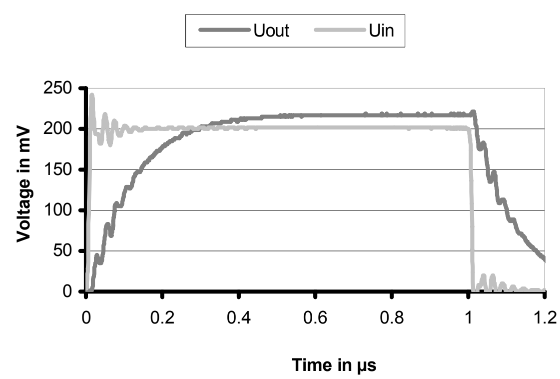

***Figure 11**. Step response of the printed RC-low-pass filter*

Figure 11 shows the measured step response, the corresponding time constant amounts to $\tau_m = 115$ ns. Although there are slight deviations caused by the capacities of the measuring setup, the characteristics prove a low-pass filter behavior.

Continuing this investigation, a Bode-diagram (**figure 12**) is recorded. The characteristics of an almost steady amplification of one up to the cut-off frequency and a decay of 20 dB/decade for higher frequencies are specific for a first-order low-pass filter. Thus, the functionality of the circuit is verified. The measured cut-off frequency of 1.5 MHz is almost equal to the calculated cut-off frequency of 1.6 MHz.

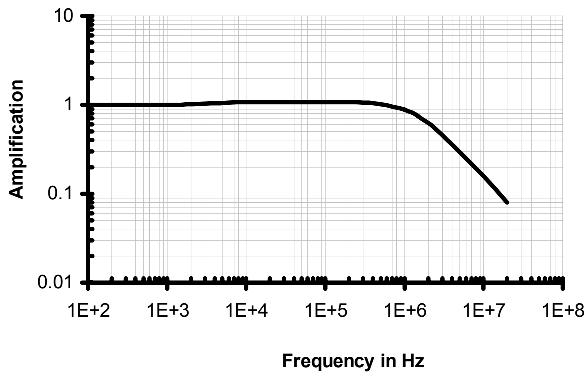

***Figure 12**. Bode-diagram of the RC-low-pass filter*

Conclusions

A low viscosity ink with a high solid substance amount that dries easily on substrates and shows no sedimentation appears to be perfect for electronic applications. In practice, it is hardly possible to realize all these requirements with the particles which are common for the fabrication of functional electronics. However, with the knowledge of the most important parameters of ink composition and their interaction, it is possible to design inks for a wide range of particles which show sufficient stability and which are reliable for inkjet printing. The printing samples proved the inkjettability of the stabilized inks and the possibility to produce functional electrical circuits using inkjet technology.

References

[1] A. Albertson, "Combined manufacture method for high density LTCC-substrates: thick film screen-printing, ink-jet, post-firing thin-film processes and laser-drilled fine-vias," Proceedings 4th International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Munich, April 2008

[2] C. Dossou-Yovo, N. Bernardin, R. Noguéra, M. Lejeune, "Manufacturing of High Resolution Water-based Ceramic and Metal Materials Using Accurate Inkjet Printing Device" Proceedings 4th International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Munich, April 2008

[3] U. Currle, K. Krueger "Factors Influencing the Conductivity of Inkjet Printed Silver Lines", Proceedings 2nd International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Denver, April 2006

[4] U. Currle, R. Moebius, K. Krueger "Characterisation of the Dispersion Process of Functional Inkjet Inks", Proceedings 4th International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Munich, April 2008

[5] U. Currle, K. Krueger, "Observations on Particle Loaded Silver Inks", 16th European Microelectronics and Packaging Conference, Oulu, Finland, June 2007

[6] D. Cibis, "DoD-printing of conductive silver tracks", Proceedings 1st International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Baltimore, April 2005

Author Biography

Ulrike Currle received her degree in cybernetic engineering from the University of Stuttgart in Germany. Since 2005 she has been working at the Institute of Automation Technology at the Helmut-Schmidt University in Hamburg, Germany. Currently she is in the final year of her PhD. Her research field is the design and characterization of particle inks for microelectronic applications with special focus on sedimentation, stabilization, dispersion, rheology, surface properties and printability.