Special Phenomena in Multilayer Deposition of Functional Particle Inks

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Abstract

The inkjet deposition of silver particles has been subject to many studies during the last years often taking in account the minimization of the line width and the realisation of conductive structures on temperature sensitive substrates. Beside fine lines on temperature sensitive substrates, inkjet printing of block shaped elements with a layer thickness of several microns on temperature resistant ceramics is of interest in printed electronics. In order to derive the required layer thickness several layers have to be printed on top of each other. As a consequence phenomena like particle flow, structured, uneven surfaces, loss of sharp edges and even pinholes and cracks occur. The study discusses theoretical aspects of ink substrate interaction and highlights the influence of the organic composition of the ink on the appearance of the printed multilayer structures as well as the effect of different ceramic substrates on the printing result. Several characteristic phenomena related to the multilayer deposition of particle inks are identified and solutions concerning ink formulation, choice of the substrate, and processing of the ink are presented.

Introduction

Inkjet printing of functional materials respectively materials for functional inkjet printing have a great potential in the upcoming years according to the market forecast 2009-2016 published by NanoMartkets in November 2008 [1]. In this report micro-electronics is identified as one of the main fields of interest. Current studies on inkjet-printing in microelectronics focus mostly on the realization of narrow silver lines [2,3,4]. However, a typical microelectronic device consists of more than narrow silver lines as exemplarily demonstrated by the plate capacitor shown in **figure 1**.

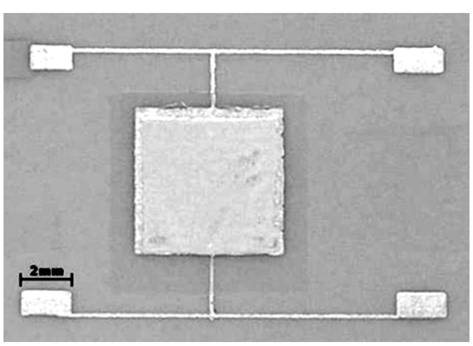

***Figure 1**. Inkjet printed plate capacitor with conductors and contacts [5]*

Besides silver lines in the range of 100 nm width and 10 µm height there are block shaped elements like capacitors' electrodes and dielectric layers with more than 1 mm width and about 10 µm height [5]. Heights of around 10 µm can be derived with inkjet technology by printing several layers on top of each other which is called multilayer printing. The great advantage of inkjet printed structures is the realization of nearly any size by combining the tiny droplets, the great challenge is the realization of perfect multilayer shapes. The multiplayer shapes are influenced by the composition of the ink, the substrates and the printing scheme - a complex interaction which is discussed in this study by investigating self-made inks with 20 to 40 wt% metal, ceramic and glass particles, different solvents and additives, printed with piezo printheads on diverse ceramic substrates.

Theoretical Aspects

The interaction of an ink droplet and a substrate can be described by the contact angle between droplet and substrate. The contact angle can be easily measured as shown in **figure 2**. A contact angle θ of zero degrees means complete wetting of the substrate.

***Figure 2.** Droplets on different substrates*

According to Young the contact angle on ideal different substrates substrates is influenced by the surface tension of the liquid σ_l, the surface energy of the solid σ_s as well as the interfacial tension between solid and liquid σ_{ls}

$$\cos\theta = \frac{\sigma_s - \sigma_{ls}}{\sigma_l} \quad (1)$$

The interfacial tension between solid and liquid is described by several models. Owens, Wendt, Rabel, Kaelble assume, that the surface tension and the surface energy consist of polar and dispersive parts (superscribed index P and D) which interact with each other [6,7,8,9]

$$\sigma_{ls} = \sigma_s + \sigma_l - 2\left(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}\right) \quad (2)$$

with $\sigma_l = \sigma_l^P + \sigma_l^D$ and $\sigma_s = \sigma_s^P + \sigma_s^D$. (3)

An extended version of Fowkes [10] takes additionally hydrogen bonds (H) of the solid and liquid in account

$$\sigma_{ls} = \sigma_l + \sigma_s - 2\cdot\left(\sqrt{\sigma_l^D \cdot \sigma_s^D} + \sqrt{\sigma_l^P \cdot \sigma_s^P} + \sqrt{\sigma_l^H \cdot \sigma_s^H}\right) \quad (4)$$

A novel approach from Oss and Good [11] distinguishes acid (+) and base (-) interactions

$$\sigma_{ls} = \sigma_l + \sigma_s - 2\cdot\left(\sqrt{\sigma_l^D \cdot \sigma_s^D} + \sqrt{\sigma_l^- \cdot \sigma_s^+} + \sqrt{\sigma_l^+ \cdot \sigma_s^-}\right) \quad (5)$$

We focused on the first approach, equation (2) and (3). Extensive investigations on particle inks prove that, at least in case of non-polar dispersion media, particles and additives do not have any detectable influence on the total surface tension σ_l of the ink. Even their influence on the dispersive and polar part of the surface tension is negligible. Thus wetting behavior is defined by the combination of dispersion medium and substrate. Knowing the polar and dispersive surface tension of both, it is possible to calculate a so-called wetting envelope, which is exemplarily shown in **figure 3**. The corresponding isolines represent constant contact angles.

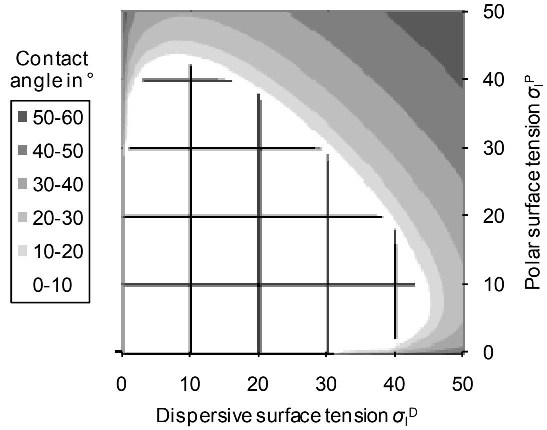

***Figure 3**. Wetting envelope of alumina*

Choosing a combination with a high contact angle stands for sharp edges in narrow line widths, in principle. However, in practice surface conditions as e.g. roughness and porosity play an important role, but even more the behavior of the particle during drying. Various phenomena may occur.

Building up functional structures

Functional structures are build up from tiny droplets as shown in **figure 4**. Lines consist of overlapping droplets and areas of overlapping lines. Lightmicroscopic pictures of inkjet printed dots, lines and areas as well as their topography are presented underneath. The ink consists of 30 wt% particles and is printed on green ceramic in one layer.

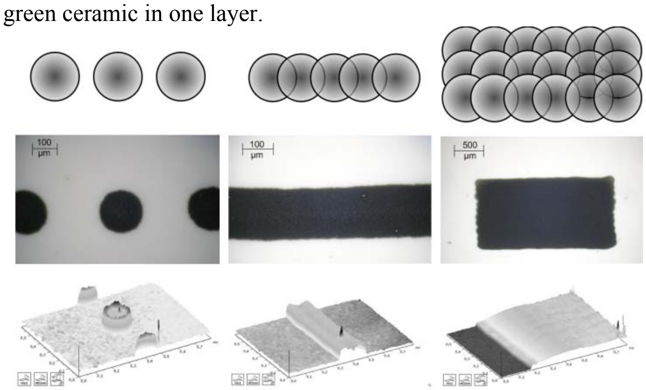

***Figure 4**. Building up functional structures*

The distance between the printed dots can be adjusted individually. If the distance is too large, the substrate is structured and not fully covered with ink, if the distance is too small, the ink tends to spread and flow. In **figure 5** the drop spacing is varied between 125 µm, 100 µm and 75 µm. The drop distance has a significant influence on the appearance of multiplayer structures. The best results can be obtained with a resolution that guarantees in the first layer a closed area without spreading.

***Figure 5**. Influence of the drop spacing or resolution on structure appearance*

After printing the areas need to dry. The drying time is mainly influenced by the temperature depending vapor pressure of the solvents but also by the specific solvent surface load as well as the substrate and the layers underneath, respectively. The areas dry from the outbound towards the center as illustrated in **figure 6**.

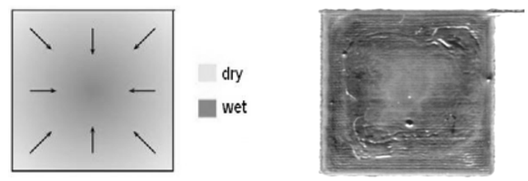

***Figure 6**. Drying procedure of a block shaped element*

The height of a printed structure is adjusted by printing one layer on top of each other. In **figure 7** the printing result after one layer, after two layers and after three layers is shown. Each layer is dried before printing the next. While the light microscopic pictures show no significant difference, the topography reveals the increasing height but also the lack of sharp edges.

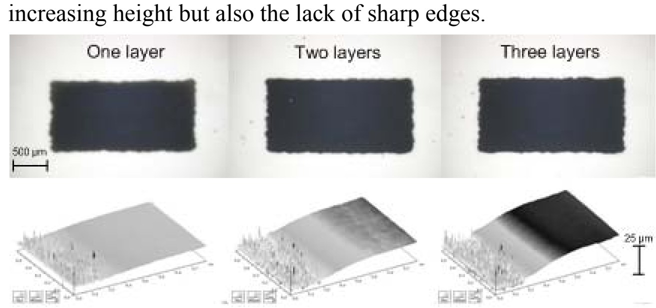

***Figure 7**. Multilayer printing*

The shape of the printed layer is influenced by the substrate and/or by the previously printed layer underneath. This layer can consist of the same material or a different one respectively, e.g. the dielectric layer between silver electrodes of a capacitor.

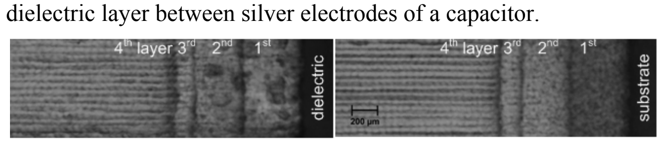

***Figure 8**. Influence of the layers underneath*

In **figure 8** the effect of different layers on the printing result can be seen. The left picture shows one to four layers of silver ink printed on previously deposited material (dielectric layer). In the right picture the same layers are printed on pure alumina substrate. The first layer behaves unsurprisingly different. With increasing layer thickness the shape becomes more dependent from the printed layers of the current ink than from original layer or substrate underneath.

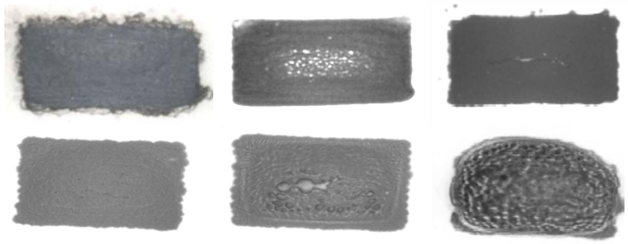

***Figure 9**. Various multilayer phenomena*

In **figure 9** several undesired multilayer phenomena of several inks on different ceramic substrates are summarized. On the top left a typical drying phenomena is presented. The edges of the structure are strongly blurred. This effect often appears on sintered ceramics. Next the appearance of pinholes and cracks is shown. This effect is likely with green ceramics.

The influence of the ink amount on the shape is demonstrated on the bottom pictures. The left picture shows one layer followed by two layers printed without drying in between. The right picture demonstrates additionally spreading caused by too small drop distances.

Influence of additives and solvents

In [12] we already reported the effect of different additives and solvents on the printing result of silver lines. In **figure 10** all silver lines are printed in the same way in five layers without drying in between on a green ceramic. The solid substance amount is 30 wt%. The left line consists of a combination of terpineol and a polymeric dispersant, the line in the middle of a combination of terpineol and ethyl cellulose and the line on the right of a combination of ethyleneglycolmonobutylether and ethyl cellulose. The effect of different additives and solvents on the shape of the line is significant. However, this effect cannot be derived from surface tension data.

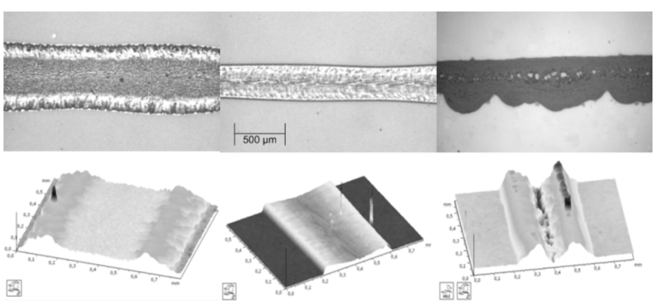

***Figure 10**. Effect of different additives and solvents*

In **figure 11** inks based on diethyleneglycolmonobutylether-acetate (DEGMBEA), diethyleneglycolmonobutylether (DEGMBE) as well as ethyleneglycolmonobutylether (EGMBE) are printed in the same way on sintered ceramic in three layers with drying between the layers. The substrate temperature is 80 °C, the additive is ethyl cellulose and the solid substance amount is 30 wt% for all inks. The shape differs significantly with different solvents. On the bottom line the profile of one up to four layers is shown.

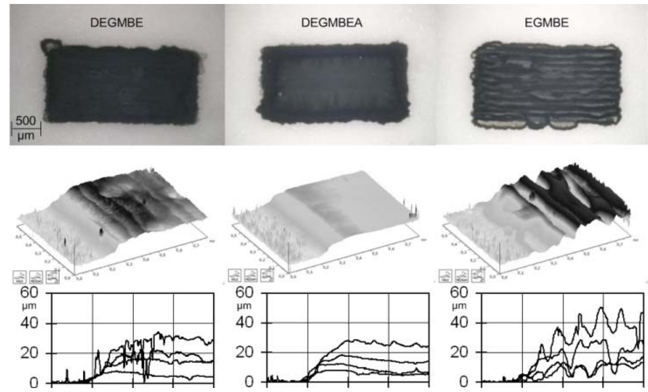

***Figure 11**. Effect of different solvents on sintered ceramic substrate*

The inks presented in figure 11 are additionally printed in the same way on unheated green tape. The printing result in **figure 12** is completely different but also reveals the effect of different solvents on the shape of the edges and the surface structure.

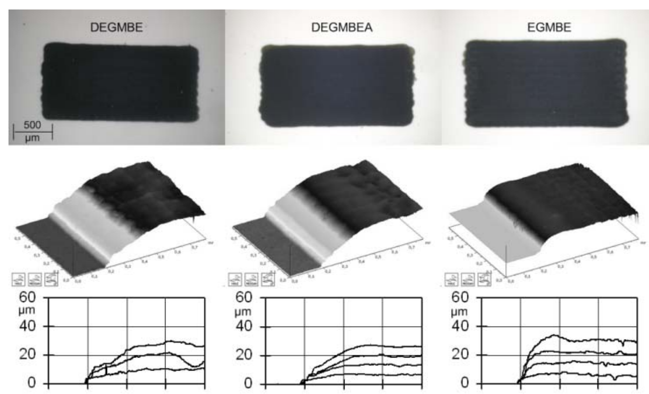

***Figure 12**. Effect of different solvents on ceramic green tape*

Printing on different ceramic substrates

The same ink can cause very different effects on different substrates. In **figure 13** the same ink is printed on three different green tapes (A, B, C). The individual behavior of the ink on the substrate can already be seen with single dots.

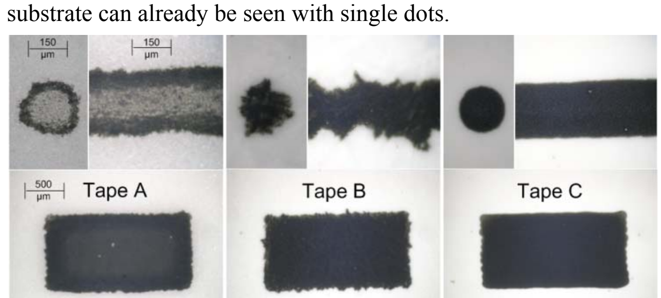

***Figure 13**. Printing on different green tapes*

In **figure 14** some extreme defects caused by the same ink on different green tapes are shown. All shapes consist of three layers and the bottom shapes consist of two layers but have further on a reduced distance between the dots that the same ink amount is applied. The defects are characteristic for each ink-substrate combination.

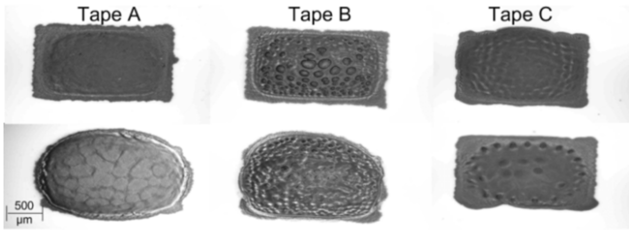

Figure 14. Defects related to different green tapes

Ink mixing

Shape properties can be influenced by combining different inks with characteristic properties. In **figure 15** an ink which causes an uneven surface is combined with an ink with a more even surface resulting in a less uneven surface.

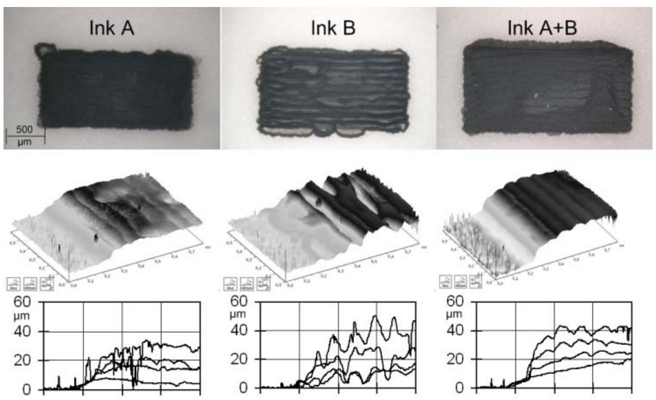

Figure 15. Influencing shape properties by mixing inks

In **figure 16** an ink which causes flat edges is mixed with an ink that causes superelevated edges resulting in a combination of shape properties of both inks. Ink mixing allows for defined shape performing.

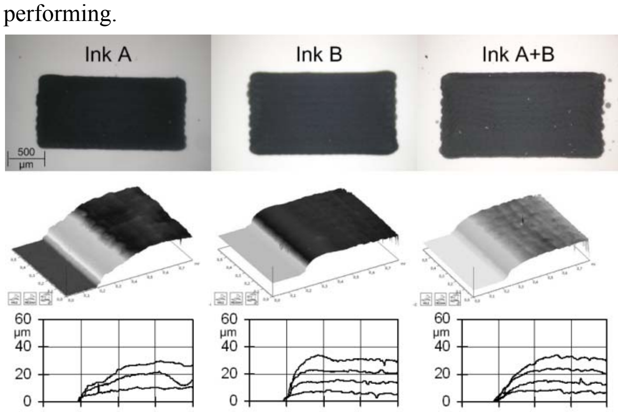

Figure 16. Influencing shape properties by mixing inks

Conclusions

The performance of block shaped elements depends on the inks, substrates and printing scheme. In **figure 17** the influencing factors are summarized. If the printing result is not satisfying, the easiest way of changing the shape is by changing the printing scheme, e.g. adapting the dot distance and the drying conditions. If the adaptation of the printing scheme does not lead to the desired result one might change the substrate if possible. Otherwise the ink composition needs to be adapted to the requirements of the substrate. As a result perfect multilayer shapes of block shaped elements can be derived.

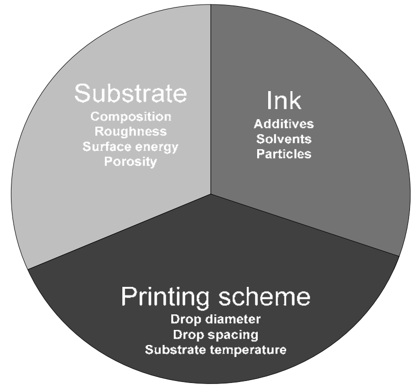

Figure 17. Control parameters

References

[1] "Materials for Functional Inkjet Printing: A Market Forecast 2009-2016", NanoMarkets, November 2008

[2] 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", 4th International Conference on Ceramic Interconnect and Ceramic Microsystems Technologies, Munich, April 2008

[3] Perelear, J.; Hendriks, C.E; Reihold, I.; Eckardt, R.; van Osch, T.H.J.; Schubert U.S.: "Inkjet Printing of conductive silver tracks in high resolution and the (alternative) sintering thereof" 24th International Conference on Digital Printing Technologies, Pittsburgh, 2008, p. 697-701

[4] Hendriks, C.E.; Smith P.J.; Perelaer J.; van den Berg, A.M.J.; Schubert U.S.: "Invisible Silver Tracks Produced by Combining Hot-Embossing and Inkjet Printing" Advanced Functional Materials 18 (2008), p. 1031 ff

[5] Currle, U.; Waßmer, M.; Krüger, K.: „Particle Inks for Inkjet Printing of Electronic Components"; 24th International Conference on Digital Printing Technologies and Digital Fabrication, Pittsburgh, 2008, p. 702-706

[6] Fowkes, F.M.: "attractive Forces at Interfaces", Industrial and Engineering Chemistry 56 (1964), No. 12, p. 40-52

[7] Owens, D.; Wendt, R.: "Estimation of the Surface Free Energy of Polymers. J. Appl. Polymer Science 13 (1969), No. 8, p. 1741-1747

[8] Rabel, W.: „Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren", Farbe und Lack 77 (1971), No. 10, p. 997-1005

[9] Kaelble, D.H.: "Dispersion-Polar Surface Tension Properties of Organic Solids", J. Adhesion 2 (1970), p. 66-81

[10] Fowkes, F.M.: "Contact Angle, Wettability and Adhesion", Advances in Chemistry Series No.43, ACS, Washington 1994

[11] Loeb, Schrader, "Modern Approaches to Wettability – Theory and Applications", Plenum Press, New York, 1992, p. 1-27

[12] Currle, U.; Krüger, K.: "Observations on Particle Loaded Silver Inks", European Microelectronics and Packaging Conference, Oulu, 2007

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Author Biography

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