Improving Performance of Laser-Printed Conductive Silver Lines

Dustin Büttner
(buettner@hsu-hh.de, Phone: +49 (0)40 6541 2254, Fax: +49 (0)40 6541 2004)
Klaus Krüger
(klaus.krueger@hsu-hh.de, Phone: +49 (0)40 6541 2722, Fax: +49 (0)40 6541 2004)
Institute of Automation Technology, Helmut Schmidt University / University of the German Armed Forces, Holstenhofweg 85, 22043 Hamburg, Germany

Abstract

Within the last decade, large efforts were made to implement digital printing as a production method for printed electronics. Especially in production of thick-film electronics, innovation is pushed forward to overcome the lacks of established screen-printing regarding flexibility and tooling. Besides the numerous approaches in using ink-jet printing for printed electronics, researchers at Helmut Schmidt University already showed huge progress in applying electrophotography ("laser printing") as a method to print conductive silver lines in order to form a conductive layout for thick-film circuits.
Electrophotography is a solvent-free method, able to directly print silver toner onto ceramic substrates, forming a conductive line after firing. Benefits are high speeds and flexibility and a huge potential regarding precision. Now, after the feasibility of the method was proven and even functional conductive layouts like RFID coils were printed, the next steps have to be taken towards developing electrophotography to an applicable method in a thick-film production process.
Thus, this paper describes the efforts in improving the method's performance. Different kinds of silver particles are tested towards their possibility of forming a silver toner. The resulting silver lines are examined regarding conductivity and printing precision. Also, surface treatment of substrates is considered as a method to reduce the number of required print cycles. Corresponding tests are performed. Furthermore, different firing profiles are tested towards their influence onto the resulting silver lines. Combining the results of these examinations, the performance of conductive silver lines could be improved significantly.

Keywords: Electrophotography, Conductive Silver Lines, Printed Electronics, Thick-film Circuit

Introduction

Electrophotography ("laser printing") is a frequently used printing method in our everyday life. It is a highly developed and widespread technology in graphic and office applications. Nevertheless, it is rarely considered regarding functional printing, especially printed electronics.

Early research showed that approaches to use electrophotography (EP) in that field had to deal with limitations in printing conductive materials such as silver or copper. They either were not successful [1], not far enough developed [2] or tried to avoid direct print of conductors [3]. Patents to directly print conductive materials in order to form an electronic circuit exist [4, 5], but due to the fact that so far no successful results were published, the main problem in printing a conductive layout still could not be overcome: The fact, that a toner must contain conductive material to form a conductive layout, but although must not be conductive during the EP process. Thus, EP could not yet be established as a digital printing method for conductive circuitry, and therefore, only ink-jet printing is considered as a serious contender of the still undoubted screen printing.

Since three years, researchers at Helmut Schmidt University (HSU) in Hamburg, Germany, are successfully taking this challenge to develop EP as an applicable alternative in digital printing of electronics.

Prior Studies and Main Focus

Despite the mentioned issues, the challenges in printing conductive powder in a electrophotographic system could be overcome by developing a method to coat silver particles with polymer before they enter the toner production process [6]. So far, the so-coated silver particles yielded two toners, C02 containing flake-shaped particles, and C03, containing spherical particles. Just as all toners in this study, they are tested using a printer prototype, developed by CTG PrintTEC in Alsdorf, Germany. In its two-component developer system, the silver toner particles are mixed with an off-the-shelf carrier to generate their charge. This flexible and robust printing system has proven its suitability to print conductive silver lines in numerous experiments performed prior [6, 7, 8].

Using this printer, C02 shows fair results in printing on fired ceramics, but yields serious problems when printed on green tape. Traverse cracks occur and no continuous conductive lines can be achieved [8]. To overcome this issue, C03 was developed. Besides basing on spherical particles, an improved coating was applied and a different type and larger amount of glass was added to the toner in order to improve its adhesion to green tape. C03, whose charge distribution is displayed in **Figure 1**, shows outstanding results in printing a functional conductive layout, on ceramics as well as on green tape [8].

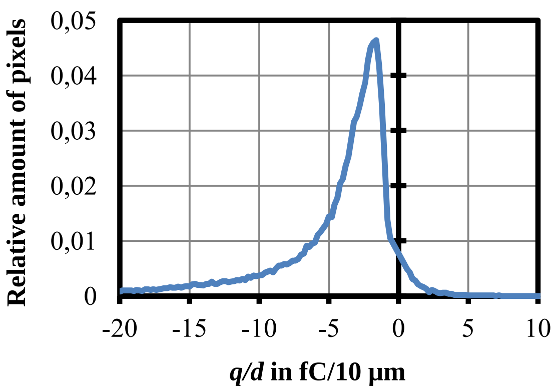

Figure 1: Charge distribution of C03 toner (mean *q/d* value of -5.0 fC/10 µm, between 1.7 and 3.3 % of positively charged particles) [6]

Nevertheless, some important issues could not be solved yet. First, the root cause for the traverse cracks is still unknown due to the manifold changes performed when comparing C02 to C03. Second, besides the good performance of silver lines presented in prior publications, research did not yet yield the desired conductivity after a single printing cycle, which is essential for an industrial production process. Hence, this paper is focused on approaching these issues and therefore developing electrophotography to a serious alternative in printed electronics.

Development of C04 Toner

A new toner called C04 was developed. Purpose of this development is to investigate the influence of toner components on printing quality. Both toners, C03 and C04, are third generation toners which are specified by an improved coating containing a higher amount of polymer than in second generation C02 toner. Furthermore, instead of regular glass, LTCC-optimized glass is added to the toner mixture in order to improve the silver's adhesion to the ceramic substrate after firing.

Both toners have identical recipes, but C03 is based on spherical silver particles and C04 is based on flakes. This approach offers the opportunity to examine the root cause for the traverse cracks, which are either caused by the particle shape or the kind of glass added. Moreover, testing an additional, flake-based third generation toner yields further knowledge about silver toner behavior in an EP system.

Figure 2 shows the charge distribution of C04, measured with the EPPING *q*-test [9]. The higher peak than in Figure 1 indicates a more homogenous charge of the toner. Nevertheless, the mean *q/d* value is a little lower than C03's. Also, a slightly higher amount of undesired positively charged particles can be noticed.

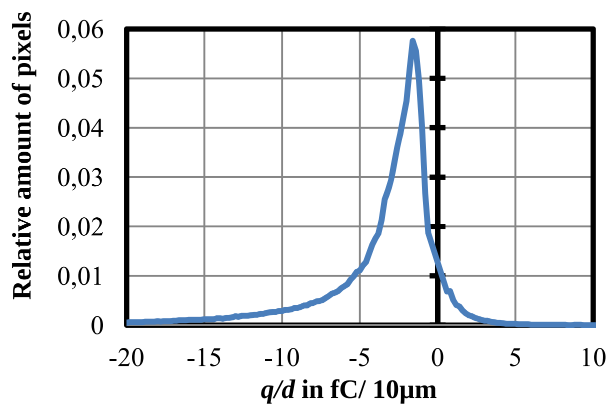

Figure 2: Charge distribution of C04 toner (mean *q/d* value of -4.5 fC/10 µm, 5.2 % of positively charged particles)

Generally, the toner behaves well inside the before mentioned printing system. No problems such as system shutdowns caused by short-circuit or failures of single printing cycles occur. The printed layouts have a good optical density and shape.

Comparing the toner with the other silver toners developed at HSU yields interesting results. As **Figure 3** shows, C04 toner results in a significantly higher transfer amount compared to older toners when printing a standardized image on green tape.

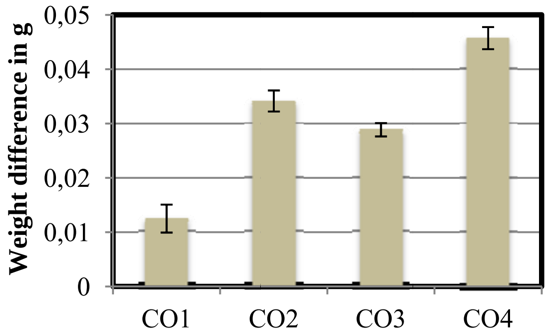

Figure 3: Deposition of different toners on green tape; weight difference between green tape before and after printing; indicators show standard deviation

Interpretation of these results has to consider the impact of several toner properties. The amount of silver (wt %) within the toners is equal in C04 and C03 toner, C02 contains a negligibly higher amount. First of all, results show a huge difference between first generation C01 toner and second and third generation follow-on toners, what underlines the success of toner coating already published before [6]. Furthermore, a significant, but not as huge improvement from second generation C02 towards third generation C04, both containing flake-shaped silver particles, can be noticed. This validates the improved coating applied to third generation toners.

The results also indicate a significantly better transfer of flake-based C04 toner compared to spherical-based C03 toner. Actually, the transferred toner weight is exceeded by a factor of approximately 1.5, which is very remarkable keeping in mind that C03 has a slightly higher mean charge. A possible reason for that phenomenon could be the higher amount of positively charged particles which create undesired background on the substrate. But the shape of the printed layout and optical assessment of the printed tapes make this conclusion seem very unlikely, especially considering the large difference between both results (factor 1.5).

A detailed investigation of this result is necessary, especially when taking into consideration that C02 also shows better transfer than C03 in this experiment. As mentioned before, C02 shows massive lacks in performance, especially the occurrence of traverse cracks. Therefore, printing silver lines and examining their performance will yield further information to evaluate the toners.

Printing and Cofiring Conductive Silver Lines

In the next step, C03 and C04 are used to print silver lines on green tape as well as onto already fired ceramics. To examine their performance on green tape, silver lines are printed onto a 2×2 in^2 green tape with one, four and ten printing cycles. Desired line widths of 0.2, 0.5 and 1.0 mm are applied, but as former studies showed, the actual width of such lines may vary [7]. Afterwards, tapes are fired with a profile using a 5 °C/min heating rate up to a 3h 400 °C burnout, which is followed by another 5 °C/min heating up to a maximum temperature of 875 °C with a 15 minute dwelling time. Afterwards, substrates are cooled down also with a 5 °C/min rate. Examination of several firing profiles show that this profile delivers better results than straight heating up to maximum temperature, but also further optimization regarding rate and burnout is possible and should be part of future studies.

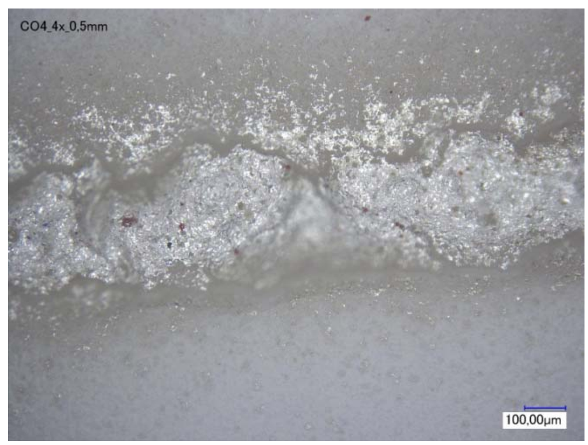

Figure 4: C04 silver lines, nominal line width 0.5 mm, printed on 2×2 in^2 cofired ceramic, four printing cycles

After firing the substrates, optical condition of the lines is examined as well as their conductivity. The results using C04 are unsatisfying. As **Figure 4** shows, the traverse cracks known from C02 also occur with C04.

Cracks are not as severe as the ones from C02 silver lines, but they are severe enough to create a high failure rate on conductivity of the lines. None of the single cycle lines are conductive (which is not unusual because still several print cycles are necessary with all toners). Failure rates and square resistance of silver lines are displayed in **Table 1** (12 (1.0 mm) respectively 18 lines printed).

Table 1: Failure rate and mean sheet resistance of cofired C04 silver lines

Print Cycles	Line width in mm	Failure rate in %	R_{sq} in Ω
4	1.0	67	10.8
	0.5	78	10.4
	0.2	67	10.7
10	1.0	50	11.7
	0.5	17	9.2
	0.2	11	7.8

Applying 10 printing cycles, results get into an acceptable, but not satisfying range. Taking a look at **Figure 5**, the obvious reason for these results is identifiable.

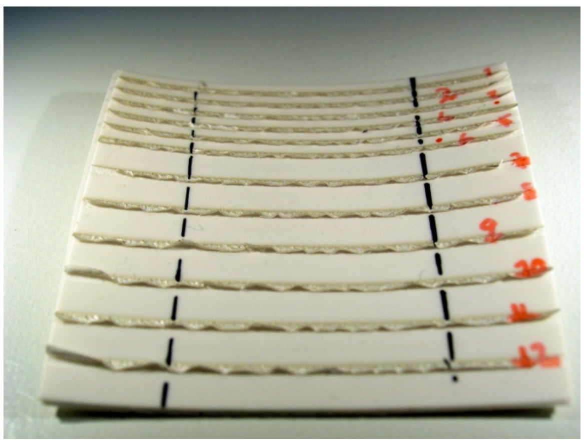

Figure 5: C04 silver lines on 2×2 in^2 cofired ceramic, nominal line width 1.0 mm, 10 cycles

The silver lines do not adhere to the substrate in a sufficient manner. They have loosened from the ceramic surface during firing process. Lines are thick and have a continuous high density, but cracks occur and adhesion is unsatisfying. Thus, the problems occurring with C02 could be eased, but not solved with applying third generation coating to the silver particles.

Table 2: Failure rate and mean sheet resistance of cofired C03 silver lines

Print Cycles	Line width in mm	Failure rate in %	R_{sq} in Ω
4	1.0	0	8.0
	0.5	0	9.6
	0.2	0	10.2
10	1.0	0	13.5
	0.5	0	8.5
	0.2	0	8.1

This gets even more obvious when comparing results with the ones of C03. Also, no conductivity could yet be achieved after a single printing cycle. However, as the results in **Table 2** show, no failures at all were noticed after four and ten printing cycles. A variation in square resistance is noticeable; it goes along with wide spread values measured. This variation comes with most cofired silver lines printed yet and is an obvious side-effect of the not yet optimized process. But still, every single printed line is conductive and optical assessment of the silver lines also yields a more satisfying impression, as **Figure 6** shows.

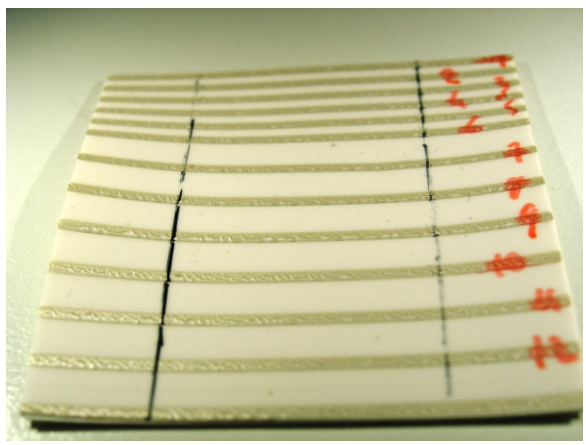

Figure 6: C03 silver lines on 2×2 in^2 cofired ceramic, 1.0 mm, 10 cycles

The lines adhere much better to the substrate compared to C04 lines and no traverse cracks can be noticed. Also, defects in lines occur, but as **Figure 7** shows, no disconnections can be noticed and a completely conductive line with sufficient density is formed.

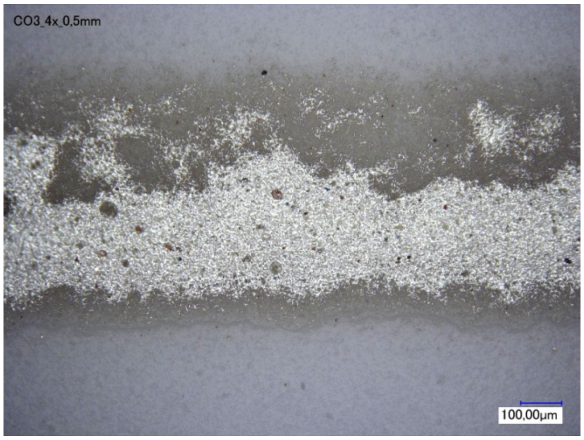

Figure 7: C03 silver lines, nominal line width 0.5 mm, printed on 2×2 in^2 cofired ceramic, four printing cycles

Printing and Postfiring Conductive Silver Lines

To gain further knowledge about the toner's performance, C03 and C04 silver lines were printed on already fired ceramics. In advance, it can be stated that the results presented so far can be confirmed by these tests.

Table 3: Failure rate and mean sheet resistance of postfired C03 and C04 silver lines (0.5 mm width, n=6)

Print Cycles	**C03**		**C04**	
	Failure rate in %	**R_{sq} in Ω**	**Failure rate in %**	**R_{sq} in Ω**
1	100	N/A	100	N/A
2	50	45,2	100	N/A
3	0	10,5	67	20.0
4	0	8,6	17	20,8
5	0	5,7	33	11,9
6	0	6,9	67	13,2
7	0	5,3	17	9,4
8	0	5,0	17	8,7
9	0	3,7	100	N/A
10	0	3,9	0	6,9

Silver lines with one to ten printing cycles are printed on the ceramic and fired applying the following profile: 5 °C/min heating rate up to 875 °C, a 15 min dwell at that temperature followed by a cool down at same rate. Although this profile is not optimized, only little effect on the silver lines can be noticed when varying fire profiles of the postfiring process. As an example for the tests performed, failure rates and mean sheet resistance of 0.5 mm lines are displayed in **Table 3**.

Again, C04 silver lines fail much too often and show insufficient conductivity, while C03 lines are realized reliably and show the expected change of conductivity with increasing number of print cycles. Results of C04 lines are very inhomogeneous. Especially the total failure after nine printing cycles is disturbing. Surely, this should be considered as an outlier due to external circumstance like a printer failure or an operator's error. Nevertheless, such a failure never occurred with C03, neither in this test series, nor in other experiments performed. Thus, it indicates the vulnerability of the bad shaped C04 silver lines.

A close look at the silver lines (example shown in **Figure 8**) shows the problems of C04: Very inhomogeneous, defected and broken lines. Obviously, the silver particles do not adhere to each other very well; respectively do not connect to the substrate as desired. Earlier test with C02 toner showed that a higher firing temperature unfortunately cannot ease this problem.

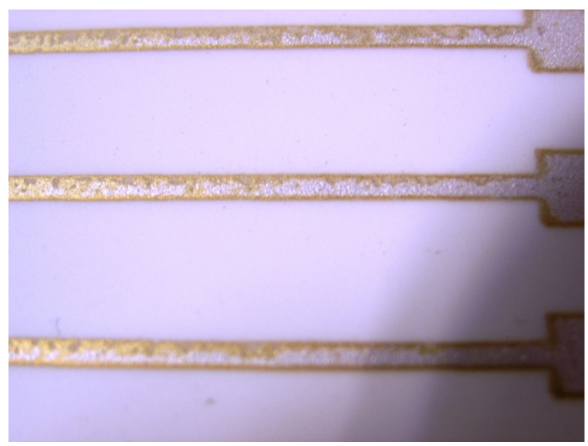

Figure 8: C04 postfired silver lines, seven printing cycles, nominal line width 1.0 mm

C04 lines do look worse compared to the C03 silver lines displayed in **Figure 9**. These lines are very homogenous and show high density, no obvious defects occur.

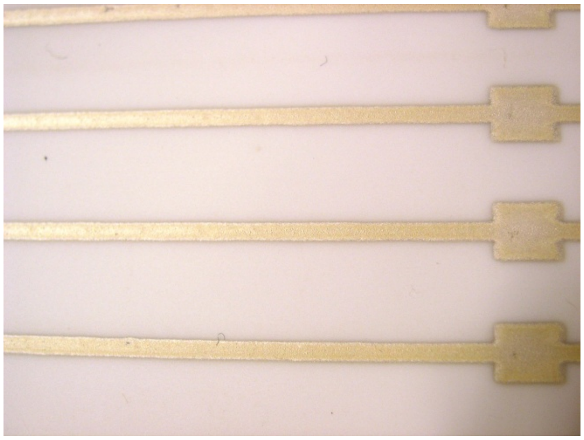

Figure 9: C03 postfired silver lines, six printing cycles, nominal line width 1.0 mm

Hence, flake-based C04 toner does not meet the requirements. Neither in a cofiring, nor in a postfiring process, can acceptable results be achieved, while sphere-based C03 toner performs very well in both processes. C04 failure rates vary in an unpredictable pattern, while C03 forms reliable lines after two to three printing cycles. Nevertheless, neither of them could yet achieve desired conductivity after one printing cycle.

Transfer Improvement by Substrate Treatment

During the development of EP to an industrial production process, conductivity after a single printing cycle was always considered a major milestone. To improve toner transfer, besides major toner research, printer optimization and substrate modification were accomplished [8]. A consequent next step is to adapt surface properties of the substrate.

This is approached by depositing brine on the substrate's surface in order to manipulate its properties. Most promising approach is brine delivered by the printer manufacturer (CTG PrintTEC), which is based on sodium chloride. It is brushed onto the surface of green tape as well as onto fired ceramics. **Figure 10** shows a comparison of transfer of C03 silver toner on treated and untreated green tape.

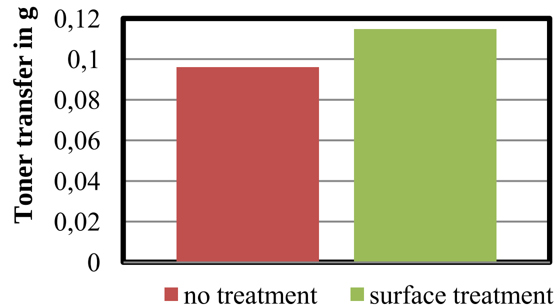

Figure 10: Deposition of C03 toner on green tape (standardized layout, mean value of ten tapes, standard deviation negligible)

Thus, a significant increase of toner transfer is detectable when surface treatment is applied. As an explanation, the electrical properties of sodium chloride improve the chargeability of the substrate which is beneficial for the printer's transfer mechanism. Another simple explanation also might be that the surface seems to be a little gluey after the treatment, which might yield a better adhesion of toner particles to the substrate. Either of these explanations should be considered, which also includes that both might complement each other and therefore improve toner transfer. However, the improvement of transfer is further tested by printing silver lines onto coated green tape as well as onto coated ceramic. Afterwards, substrates are fired in a cofiring respectively a postfiring process applying the firing profiles described before.

Printing results on green tape are not satisfying yet. Despite the increase in transfer, no sufficient amount of silver of both toners is deposited to form a conductive silver line after one printing cycle. However, disappointment is overcome when taking a look at the results of the postfired silver lines presented in **Table 4**.

Table 4: Failure rate and mean sheet resistance of postfired silver lines on surface-treated ceramics, one printing cycle

Toner	Line width in mm	Failure rate in %	R_{sq} in Ω
C03	1.0	0	41.8
	0.5	50	38.1
	0.2	83	72.3
C04	1.0	17	51.5
	0.5	0	38.9
	0.2	83	68.5

For the first time, electrophotographically printed, conductive silver lines can be produced with only one cycle. Conductivity and failure rate are not yet satisfying, but the improvements made by applying surface treatment are another step in using the full capabilities of EP in thick-film technology. Remarkably, also C04 is able to form acceptable silver lines, as **Figure 11** shows.

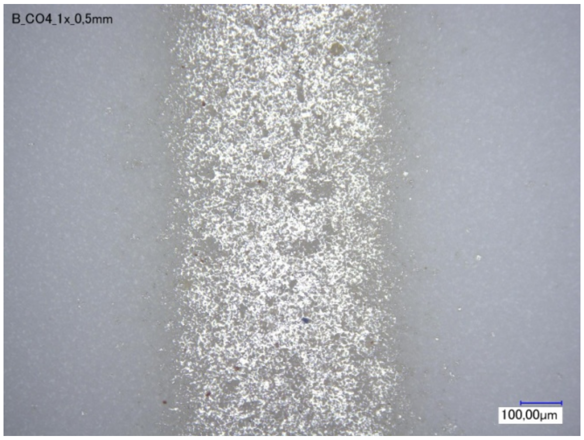

Figure 11: Postfired C04 silver line on surface-treated ceramic, one printing cycle, nominal line width 0.5 mm

The line's weak density and the obvious defects are the probable reasons for the low conductivity, but the line is remarkably well shaped and obviously dense enough to conduct at all.

As assumed with the knowledge gained prior, C03 lines still are better shaped and more dense than C04 lines, although the difference in quality is not as big as expected. Such a line is displayed in **Figure 12**.

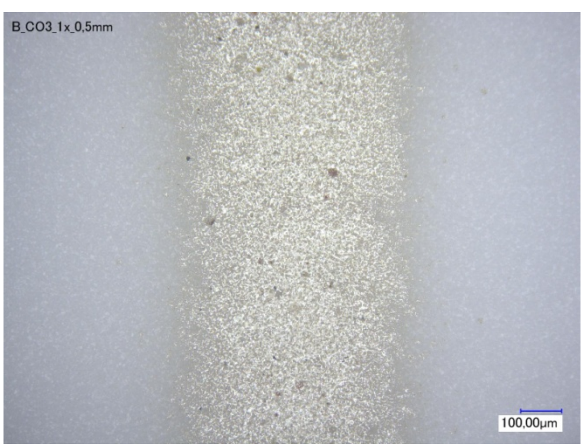

Figure 12: Postfired C04 silver line on surface-treated ceramic, one printing cycle, nominal line width 0.5 mm

Conclusions

The comparison between C02, C03 and C04 co- and postfired silver lines show that silver toner based on spherical silver particles perform better in the EP process and yield more conductive and more reliable silver lines than flake-based toners. Third generation particle coating pushes the performance of both kinds of toners, but obviously, the shape of the particles has a big influence on the toners properties.

Especially the firing process is a huge challenge for flake-based toners. This yields two future approaches: One is to prioritize the development of spherical based toners, because they are more suitable for the pegged requirements. If spherical particles shall be used despite the drawbacks, a new approach has to be developed regarding substrates and firing, in order to make particles and process fit to each other.

Furthermore, feasibility of conductivity after a single cycle is proven. This can be considered a decisive step to utilize the full potential of EP regarding resolution, accuracy and print speed.

Nevertheless, still further development is necessary. The singe-cycle line density has to be improved and the transfer process has to be optimized. Also, the surprisingly good performance of C04 after a single cycle requires further investigation. Possibly, a new approach towards flake-shaped silver can be extracted from these results, when considering that a low amount of silver obviously performs better than higher amounts.

Subsuming all of these conclusions, research took another step towards an industrial EP-based thick-film production process by identifying key factors for toner performance and pushing toner development further, complemented by new approaches towards toner transfer to substrate. Finally, the long-pursued objective of printing conductive lines after a single cycle could be fulfilled.

References

[1] J. B. Jones et al, "Printed Circuit Boards by Selective Deposition and Processing", Proc. of Twenty Second Annual International Solid Freeform Fabrication, Austin, 2011.

[2] C. Wagner, R. Patwardhan, B. Jang, M. Mahinfalah, "Electrophotographic Direct-Write for Electronics", Proceedings of NSTI Nanotech, Boston, May 2006, pp. 206-209.

[3] H. Aoki, et al, "A Study of Electrophotography Process for Manufacturing Printed Circuit Board", Proc. of NIP 20 and Digital Fabrication 2004, Salt Lake City, 2004, pp. 241–245.

[4] A. Kamada, I. Kato, N. Sakai, “Circuit Forming Charging Powder and Multilayer Wiring Board Using the Same”, US Patent # US 6,2145,508 B1, April 10th, 2001.

[5] K. Ueda, I. Nakamura, K. Sakurada, “Process for Producing Resin-Coated Metal Particles, Resin Coated Metal Particles, and Toner for Forming Circuit”, US Patent Application # 2008/0081275 A1, 2008.

[6] D. Büttner, W. Diel, K. Krüger, “Pre-Treatment of Silver Particles as a Basis for Functional Toner”, Proceedings of NIP27 and Digital Fabrication 2011, Minneapolis, October 02-06, pp 462-465, 2011.

[7] D. Büttner, W. Diel, K. Krüger, “Digital Printing of Conductive Silver Lines: Comparison between Inkjet and Laser Printing”, Proc. ECerS XII, Stockholm, 2011.

[8] D. Büttner, B. Zobrist, A. Schönberger, D. Jung, K. Krüger, “Electrophotographic Printing of RFID Antenna Coils on Cofired and Postfired Ceramics”, Journal of Microelectronics and Electronic Packaging, Vol. 8, No. 2, pp. 58-65, 2011.

[9] A. Küttner, R. H. Epping, “Theory and Practice of a Small Toner-Charge-Spectrometer”, Proceedings of NIP 14, Toronto, 1998.