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Conductive Atomic Force Microscopy Analysis of Double Layer Inkjet Printed Electronic Structures (C-AFM)

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Abstract- The local electrical characteristics of double layer inkjet printed electronic structures were studied with conductive atomic force microscopy (C-AFM). The investigated samples were silver traces produced by inkjet printing of silver Nano ink. The silver traces were covered with different circumferences of silver ink, PEDOT: PSS ink and carbon ink. So, the samples consisted of an underlying silver layer with a conductive layer on it. Additionally, to the conventional topography analysis, the current conduction characteristics of the layers were investigated by mapping the current distribution over the topography with a nanoscale resolution. The results proved that the pass-through of current through a double layer probe of a silver trace, which is coated with a PEDOT: PSS or carbon layer is significantly influenced by the layer thickness of PEDOT: PSS or carbon layer. Nevertheless, the enhancement of the layer thickness does not lead to the same values as pure PEDOT: PSS or pure carbon layer would deliver. So coverage influences the conductivity on a low level but protect the underlying layer in a proper way against mechanical stress.

Keywords- *Conductive Atomic Force Microscopy, Printed Electronics, Inkjet Printing, Double Layer Silver Ink, Carbon Ink, PEDOT: PSS*

I. INTRODUCTION

On the one hand, we have the classical production process of a sensor, which is informed by elaborate technical processes, e.g. etch- or vacuum-processes and elaborate production conditions, e.g. cleanrooms. On the other hand, we have current developments like the Industrial Internet called in Germany “Industry 4.0”. One of the aims of Industry 4.0 is to generate a digital copy or twin of the production system and the processes, which allows the user to analyze these processes in real-time and to make predictions for the future behavior of the production system. So, Industry 4.0 is promising to avoid problems and to increase efficiency as well as effectiveness of a production. But to realize such improvements enormous amounts of data will be needed to enable such simulations. A lot of these data will be produced by sensors, which are integrated in the production process but that also means that the quantitative need of sensors will raise with the ongoing realization of Industry 4.0. Simultaneously there is an increasing cost pressure by the usage of decentral electronics noticeable, which leads in conclusion to the necessity of innovative and flexible processes to produce sensors and electronics. Generative processes about materials on nanoparticle basis or in other words the inkjet printing of electronics is one of the processes which can enable to produce low cost sensors with short production introduction time and with the option of a direct integration into the later component. [1]

A great amount of properties, such as the electrical conductivity and its dependency from factors like the ink, the substrate, the layout, the printing conditions and the compression temperature of printed electronics out of different inks (SWCNT, PEDOT: PSS; Silver) have already been examined. Especially Dietrich and Tekath did very intensive examinations on the possible fields of application and the processing of conductive carbon inks. [2] [3] [1] [4] [5]

Even the overwriting of layers out of conductive inks with a layer out of the same ink and the resulting impact on the transparency and the resistance was already examined by Song et al. They could prove that the resistance and the transparency of a printed electronic structure decreases proportional to the number of overwrite. [3]

However, the accumulated research does not answer the question of the impact of covering or overwriting one layer out of conductive ink with a layer out of another ink. So the article in hand will deal with the following question: Which influence do different circumferences of coverage with a conductive layer have on an underlying layer of silver Nano ink, e.g. does a covering layer protect an underlying conductive layer against mechanical stress?

Therefore, we used an atomic force microscope in the conductive mode or current sensing atomic force microscopy, also called C-AFM. Especially for thin electronic films C-AFM is an outstanding tool for examining nanoscale heterogeneity in terms of electrical conductivity. [6]

Based on the literature review the following hypotheses could be formulized:

Hypothesis 1: The pass-through of current through a double layer probe of a silver trace, which is coated with a PEDOT: PSS layer is significantly influenced by the layer thickness of PEDOT: PSS.

Hypothesis 2: The pass-through of current through a double layer probe of a silver trace, which is coated with a conductive carbon layer, is significantly influenced by the layer thickness of the carbon layer.

Hypothesis 3: If the contact area is coated with a coverage of conductive ink this leads to a reduction of the current to the level of the conductive coating-layer when the coverage has an appropriate thickness.

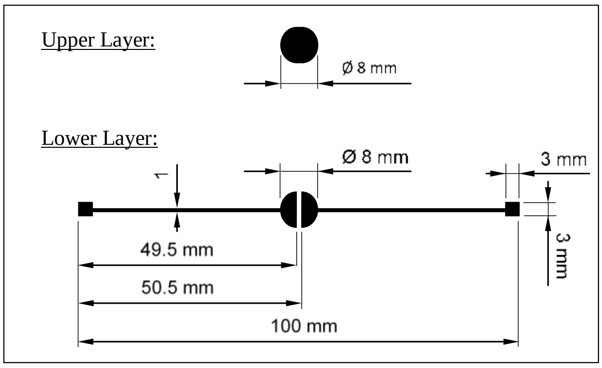

Figure 1. Design of the switching cycle test pattern (upper and lower layer)

II. METHOD

For the examination of the research question, which influence coverage of PEDOT: PSS-/ carbon-ink has onto the conductivity of printed silver layers, a C-AFM was applied as measurement-tool as well as conductive inks printed on layers as measurement samples.

We used four different types of overprinted layers to proof the above introduced hypotheses: (1) double printed silver trace without coating; (2) single printed silver trace with single PEDOT: PSS-layer-coating; (3) single printed silver trace with single conductive carbon-layer-coating; (4) single printed silver trace with double carbon-layer-coating. The layers were printed without pre- and post-treatment with a time lag of one hour between each layer-printing. Afterwards the measurements using AFM in the Spreading-Resistance-Mode were performed.

For the measurement of the conductivity a C-AFM was selected, which has the ability to collect measurement-values and to transform them into graphical topographies. A main ability is to visualize the topography of thin films on a nanometer resolution. Additionally, the C-AFM can map the local conductivity of thin films. Therefore, there is a voltage applied to the tip of the AFM and the conductive thin film (sample) is connected to the ground. So, the local current can be measured and a mapping can be created showing the local current distribution or in reverse the electrical conductivity in dependency to the respective local area. The resolution of C-AFM is as small as the tip-sample contact area. This area can be less than 20 nm. [10] [11] [12] [13]

A. Materials

The following materials were used in this study: (a) Printer - The switches were printed with the low-cost printer from Brother (Typ: MFC-J6710DW); (b) Switch Design - The switch pattern was created by using Microsoft Word 2013. Figure 1 shows the design of the upper and lower switching layer:

Layer Substrate - *Novele™* is used as substrate from *NovaCentrix*. AgIC Printing System Start Guide recommend for the above-mentioned Brother Printer the following setting: Media Type "Brother Photo Paper BP61"; Print Quality "Best"; Color Mode "Active"; Orientation "Portrait" [7] [8] Connection - The lower switching layer were connected with two connecting wires, which were glued with a standard electro-conductive glue onto the contact pads; Ink - For the printing were used the AgIC Circuit Printer Cartridge Set. In this set the silver ink has already been poured into a set of 3 *Brother LC71* (US) / *LC1240* (Europe) cartridges. Furthermore, it was used Poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) – 0.8% in H_20, conductive inkjet ink from the company Agfa-Gevaert N.V. as PEDOT: PSS ink and Resistive Inkjet Ink #3800 Series from the Methode Development Company as carbon ink.

B. Measurement

For the measurement, an easyScan 2 FlexAFM of the company Nanosurf was used. All measurements were performed in the Spreading-Resistance-Mode. Each measurement was repeated five times. The AFM does not require any pre-calibration steps for conductivity measurement. The aim of the measurement was to capture the current and the topography of the probes with due regard to the recommendations given in the manual of the measurement system. [9]

The used cantilever (PPP-EFM form Nanosensors) was coated with Platinum/Iridium. The cantilever had the following dimensions: length of 225µm; width of 28 µm: thickness of 3µm; tip radius < 25 nm. Just on radius was used for the measurements of this experiment. The force constant of the cantilever was 2.8 N/m. Furthermore, the following parameters for measurement were elected: Image Size = 10 µm, Time / Line = 1s, Points / Line = 256, Rotation = 45°, Setpoint = 100 nN, P-Gain = 3000, I-Gain = 300, D-Gain = 0 and Tip Voltage = 5 Volt (= Resistance 100 kΩ). The following illustrates all relevant settings:

Scan group	
Image size	10μm
Scan direction	Prepare...
Time/Line	998ms
Points	256
Lines	256
X-Slope	0 °
Y-Slope	0 °
Rotation	45 °
X-Pos	0 m
Global	
Measurement env...	Air
Operating mode	Spreading Resistan...
Cantilever type	PPP-EFM-SPL-Platin
Head type	EZ2-FlexAFM
Scan head	38-10-076.hed
Laser working point	29.1%
Deflection offset	-6.9%
Software ver.	3.4.0.2
Firmware ver.	3.4.0.0
Controller S/N	023-10-896
Feedback group	
Setpoint	100nN
P-Gain	3000
I-Gain	300
D-Gain	0
P-Gain2	0
I-Gain2	1000
D-Gain2	0
Tip Voltage	5 V
Feedback Mode	Free Running
Feedback algo.	Adaptive PID
Error range	4.18μm
Ampl. Ctrl. mode	Const. Drive
Module	
Controller Board	2
AFM Basic Module	3
AFM Dynamic Mo...	2
AFM Extension M...	1
Signal Module A	2
USB Module	4
Nanosurf Report	6
Spectroscopy Mo...	1

Figure 2. Setttings of the measurements for easyScan 2 FlexAFM from Nanosurf

All measurements were performed in a temperature controlled room with 22°C and 80% relative humidity. During all measurements, the AFM was in a closed chamber to protect the AFM from draught and other external influences. Layer 2 (Silver Nano Ink) was grounded during all measurements. Figure 3 shows a schematic illustration of the experimental arrangement:

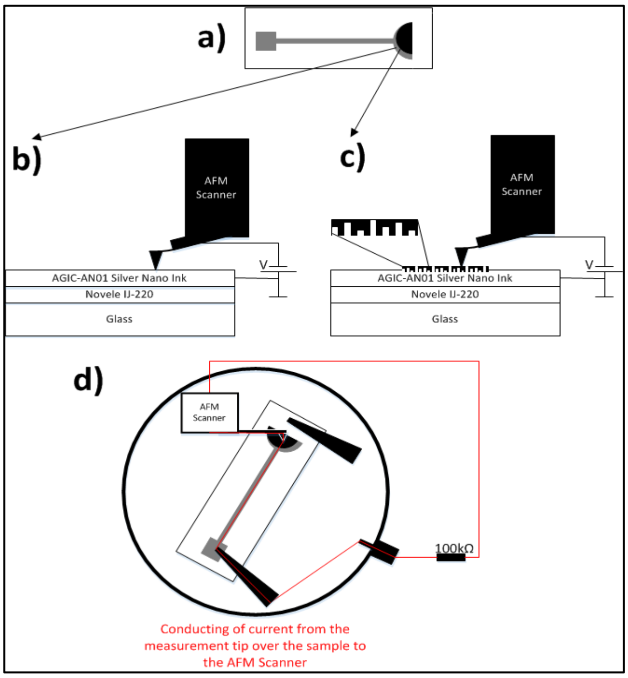

Figure 3. Experimental arrangement according to (7): a) Sample, which is placed on a carrier; b) Scheme of the C-AFM experiment on the silver area of the probe; c) Scheme of the C-AFM experiment on overwritten area of the probe; d) Illustration of the conducting of current from the measurement tip over the sample to the AFM Scanner

III. Results

The following results could be determined for the respective section. Please note, that we selected for the presentation of the results one measurement-figure out of five (test replications n = 5), which represents an average. Each measurement consists out of 256x256 points, in total 65,536 point measurements per sample with an error range = 4.18 µm, which is illustrated in figure 2.

(1) Double printed silver trace without coating: For this purpose, the topography of the silver surface and the respective Tip-Current-Mapping determined. The probe in hand delivers a mean current of 24.78 µA with a span of 54.83 µA. The maximum height difference was in span 6.093 µm, which is illustrated in figure 4:

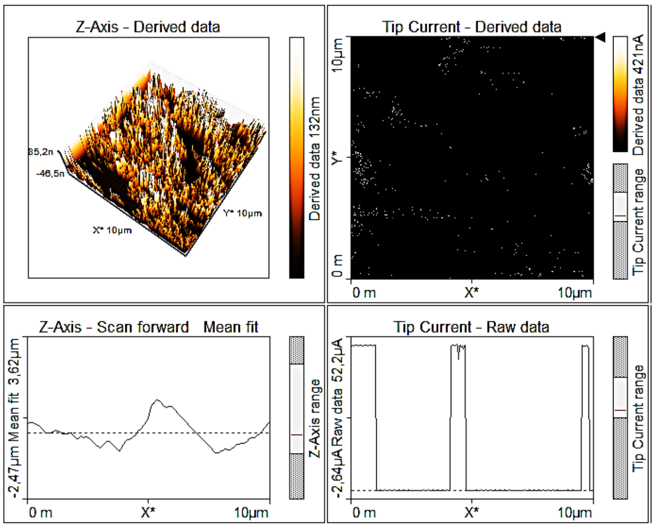

Figure 4. Measurement result of double printed silver trace without coating (easyScan 2 FlexAFM from Nanosurf); test replications n = 5

(2) Single printed silver trace with single PEDOT: PSS-layer-coating: The values exhibit a Tip-Current of 19.95 µA with a span of 44.29 µA. The height difference show in span 772.8 nm. The results shows lower tip-current values but it is to state that they are relatively high if it is considered that the second layer is a PEDOT: PSS and not a silver layer. Afterimages show the measurement results for this probe. “Tip Current – Line Fit” exemplifies the spots with strongly increased current (=white points represent points with high current). In comparison with the topography in the image “Z-Axis – Scan Forward – Line Fit” it is noticeable that the areas with high current correspond with areas of low height in the topography. The white circles mark these areas, as depicted in figure 5:

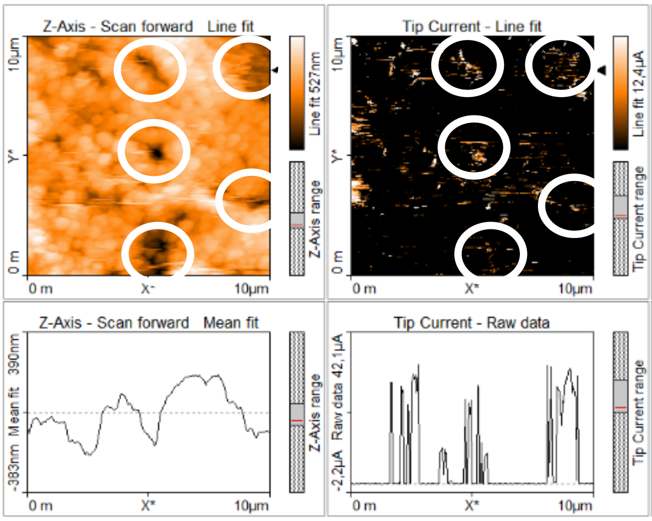

Figure 5. Single printed silver trace with single PEDOT: PSS-layer-coating (easyScan 2 FlexAFM from Nanosurf); test replications n = 5

It is assumed that in the slots respectively in the areas with low height the silver is densely and directly under the surface. This assumption was verified by the use of a 3D-laser-scanning-microscop (VK-X200) from the company Keyence, as shown in figure 6:

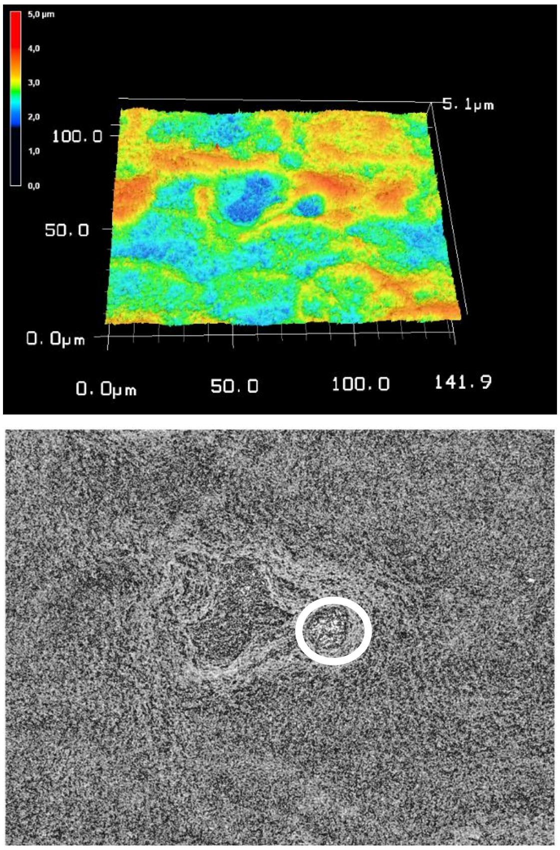

Figure 6. Full colored 3D-laser-image and as laser-image in grayscale of a single printed silver trace covered with a single PEDOT: PSS-layer (VK-X200 from Keyence)

The areas marked by the white circles in figure 6, show that the silver trace appears out of the PEDOT: PSS-layer. This means in other words, that in this area nearly a total pass-through of the current through the PEDOT: PSS takes place. In conclusion, this explains the relative high tip-current values.

(3) Single printed silver trace with single conductive carbon-layer-coating: In analogy to the above mentioned experiment a silver layer is coated with a conductive carbon layer in this experiment. The same measurement as in the experiment above were performed. The results in figure 7 show that the probe had a tip-current of 19.64 µA with a span of 43.78 µA. The height difference in span was 1.005 µm. Again, the examination of the withe spots alongside the slot, which is marked by a white ellipse. This time also the assumption can be made, that the covering carbon layer in this area is very thin and that the silver is very close under the surface, which would explain the high current indicated by the white spots, which can be seen in figure 7:

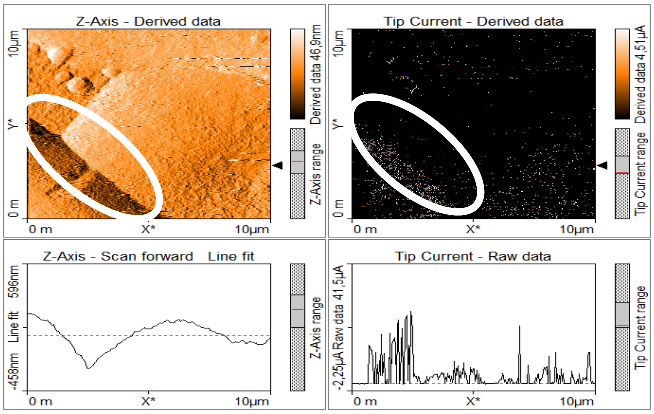

Figure 7. Single printed silver trace with single conductive carbon-layer-coating (easyScan 2 FlexAFM from Nanosurf); test replications n = 5

Surprisingly is, that the tip current values of the sample with single conductive carbon-layer-coating (see figure 7) are on a comparable level to the tip-current values of PEDOT: PSS (see figure 5). Especially if the fact is considered that carbon is a lot cheaper than PEOT: PSS. To get a deeper understanding of the interaction of different inks, a 3D-laser-scanning-microscop-examination was carried out, which is depicted in figure 8:

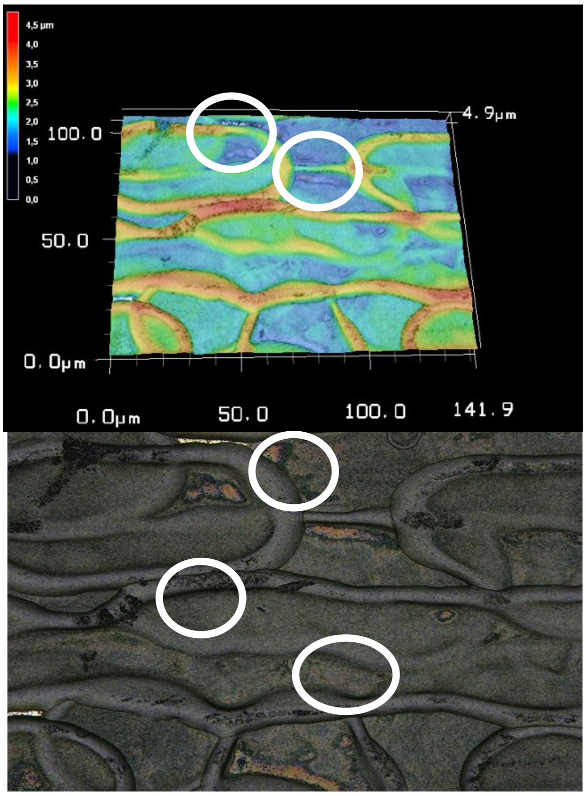

Figure 8. Full colored 3D-laser-image and as laser-image in grayscale of a single printed silver trace with single conductive carbon-layer-coating (VK-X200 from Keyence)

The results of figure 8 show, that in the white highlighted circles, the printed silver traces pierce through the carbon surface respectively that the silver traces are close under the carbon surface, which is on that area very thin. So, in conclusion this explains also in this case the relative high tip-current values. In addition to that the measurement from VK-X200 shows the good coverage of the underlying layer (= silver) with carbon which is well-known for better mechanical stress behavior.

(4) Single printed silver trace with double carbon-layer-coating: For the examination of the tip-current-behavior when a very compact and dense coverage is applied on the silver trace a measurement with double printed carbon layer was performed. The results are shown in figure 9:

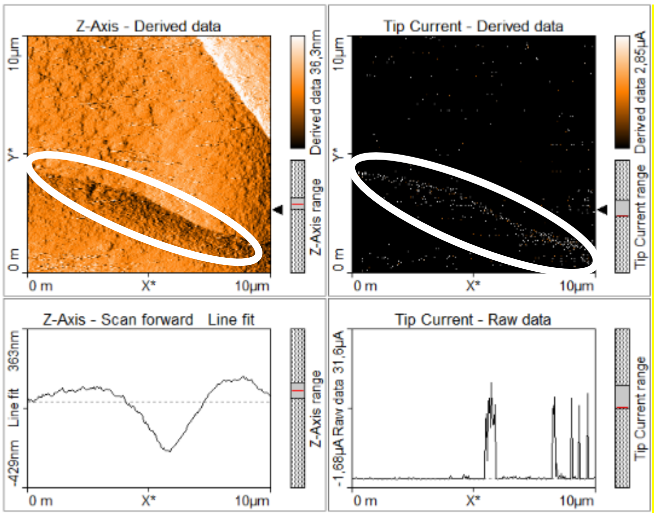

Figure 9. Single printed silver trace with double carbon-layer-coating (easyScan 2 FlexAFM from Nanosurf); test replications n = 5

Figure 9 shows a tip-current value of 14.99 µA with a span of 33.23 µA. This value is a bit lower than the previously observed value. The span of the height difference was 791.6 nm. However, in summary the same saliences, which are also highlighted by the white ellipses, could be ascertained.

IV. DISCUSSION

The results can be summarized as following: **Hypothesis 1** can be confirmed, because a thin coating of PEDOT: PSS hardly represents a barrier for the current. The respective thickness of the layer obviously influences the current, which is proved by the white spots in the slot of the respective figures.

Hypothesis 2 can be also confirmed. Surprisingly the substitution of the expensive PEDOT: PSS through the inexpensive conductive carbon was possible without a significant negative change in the current conduction. This circumstance is supported by the fact that Dietrich and Tekath showed that conductive carbon ink can even be used as a substitution for gold. [2]

Hypothesis 3 cannot be confirmed, because the doubling of the carbon layer just leads to a decrease of the current conduction to 14.99 µA. Nevertheless, this value is far away from the value of pure conductive carbon.

Based on the above mentioned results the following conclusions can be formulized:

(1) The coverage of silver traces with conductive polymers - PEDOT: PSS or carbon - in due consideration of thin layer thicknesses is possible without a significant influence on the current conduction;

(2) The application of inexpensive conductive carbon inks in comparison to PEDOT: PSS is for this special case of application possible.

For a possible practical application, this means that the coating of silver traces with different conductive inks can be a way to realize a protection layer for the silver without influencing the current conduction in a negative sense significantly. That means a layer thick enough for protection and thin enough for conduction. More precisely it is a way to cover the rather hard and brittle silver layer with a soft and flexible layer out of polymer, which is necessary to prevent mechanical instabilities occurring under mechanical stress. Similar results have already been shown by Kim et al. For them, it was able to substitute indium tin oxide (ITO) through films of AgNW/PEDOT: PSS. These films were also produced by coating and showed no change in their conductivity under mechanical stress. Furthermore, Dieterich and Tekath showed that it is possible to protect different conductive structures by overprinting them with conductive carbon ink. The major advantages of conductive carbon coatings were that carbon protects underlying conductive structures form chemical, mechanical and environmental influences, which leads to a long service life of the protected component. Besides this point the production process of conductive carbon inks is simpler and shorter as the production process of a conventional protector like gold. This means that the substitution of gold by conductive carbon leads also to significant cost savings. [14] [2]

For future examinations, it seems to be reasonable to pre- and post-treat such coverages and to examine whether it is possible to optimize the strength of electric current or not. This would pursue the examinations made by the Bavarian metal and electronic employer association through the component of covering the printed silver traces. Dietrich and Tekath already performed alike examinations but just with copper as underlying layer. So again, it should be noted, that the influence of pre- and post-treatment on the combination of silver and carbon or other conductive inks should be examined. [1] [2]

To deepen the knowledge with regard to the interaction between layer thickness, conductivity and mechanical stress it is recommended to perform further research to figure out an optimum between conductivity and layer thickness in order to achieve an optimized resistance against mechanical stress.

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