Influence of the process workflows on the electrical properties of a UV-curable polymeric dielectric for all-inkjet-printed capacitors

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ABSTRACT

Due to its inherent additive nature, non-impact deposition, accuracy in micrometer range obtained in the fabrication of passive and active printed electronic components, ink-jet printing is a relatively versatile technology. Today’s market offers many varieties of inkjet printable polymeric dielectric inks, which is the primary requirement for the fabrication of printed capacitors. When compared, the best and most obvious choice has always been ultraviolet (UV) curable polymeric dielectric inks. These inks can be printed effortlessly through the various inkjet printing systems and will not dry by evaporation and hence lead to nozzle failures. Furthermore, these inks are cured by UV radiation within a few seconds and this is a promising aspect and contributes towards roll-to-toll processing. In this paper, we discuss the all-inkjet-printed capacitors, which are developed using a nanoparticle silver ink SunTronic silver EMD5603 from SunChemicals and a UV curable dielectric ink Hyperion Pro Wet Black from Tritron. The focus of the investigation is the morphological dependence of the curing procedure on the printed UV curable dielectric layer when the time and exposure duration of the UV radiation is taken into prime consideration. It is expected that the process of curing effects the formation of the dielectric layer and its thickness. Also, it is seen that the relative permittivity of the materials changes when the curing workflow itself is altered.

Keywords: Inkjet-printed capacitors, UV curable dielectrics, dielectric material permittivity

INTRODUCTION

Inkjet printing technology offers the highest possibilities of manipulation and formation of printed functional layers [1, 2, 3, 4] due to its droplet by droplet and line by line printing process. Additionally, the post-treatment step, which converts a deposited liquid layer into a functional solid layer, defines the latter morphology of the printed layer. Well-known phenomena occurring in the deposited liquid layers are the coffee ring effect and the marangoni flow, causing material accumulations at the edges or the center of a printed layer while drying. [5, 6] As for the capacitors, the material itself, the thickness and homogeneity of the dielectric layer define the electrical characteristics and working of the printed capacitor device. [7, 8, 9, 10] The thinner the dielectric layer for a given active area, the higher is the obtained capacitance. It is defined by equation 1.

$$C = \varepsilon_0 \varepsilon_r A/d$$

Where $C$ is the capacitance, $\varepsilon_0$ is the electric constant, $\varepsilon_r$ is the relative material permittivity; $A$ is the active area, and $d$ is the layer thickness of the dielectric. The thickness of the printed dielectric
layer can be varied by changing the print resolution (drop distance or drop spacing) of the print pattern or by the deposition of multiple layers. However, if the printed sheet has even negligible differences in its homogeneity, seen for example in fluctuating layer thickness, the capacitance can be influenced negatively, and the reproducibility together with the yield might drop. This research investigates the inkjet printing and post-treatment workflows for a UV curable dielectric ink and the potential in manipulating the layer formation of the UV dielectric layer in that way, to achieve the most homogeneous and thinnest dielectric layers at the best electrical performance (capacitance and dielectric material permittivity). This will be obtained by implementing various UV curing workflows during and after printing to analyze the layer formation with for example UV curing and its effect on the thickness homogeneity. Moreover, pre-treatment techniques and their impact on the layer structure of the UV ink spreading after deposition on the substrate are studied. This research aids to achieve the best performing all-inkjet-printed capacitors by optimizing the dielectric layer formation.

“State of the Art”: There are only a few examples in the literature that have used inkjet printing for the manufacturing of metal-insulator-metal (MIM) capacitors. Bidoki et al. demonstrated thermal inkjet printing of capacitors based on desktop printers. They did not print the dielectric layer but employed the substrate (paper or PET) as a dielectric separator for printed silver layers or simply deposited identical silver lines next to each other (air as dielectric). Thus, the capacitance is comparably small (1.5 nF for a capacitor size of 45 x 45 mm²). [11] Liu et al. focused on the manufacturing of all-polymer capacitors using inkjet printing. PEDOT:PSS acted as the bottom, and top conductive layers and a polyimide precursor material dissolved in NMP (PBPDA-PD) was chosen as a dielectric material due to its high dielectric strength and excellent printability with an Epson piezo electric desktop printer. The sizes of the printed capacitors were 2 x 2 mm² exhibiting 53 pF. [10] Kang et al. manufactured all-inkjet-printed capacitors on polyimide substrates. [12] They applied silver as a conductive material and PVP and BaTiO3 as the dielectric layer with additional sintering at 210 °C for 60 min. BaTiO3 has a very high dielectric material permittivity resulting to an enhanced capacitance in comparison to PVP. [12] The best value obtained is stated as 50 pF for a capacitor size of 0.8 x 1 mm². Due to the scale of the BaTiO3 particles, a single nozzle system with 100 µm nozzle diameter was selected as the printing system. Up-scaling the single nozzle system and/or using high sintering temperature limiting the materials that can be used as the substrate [12] is disadvantageous. In a recent paper, Lim et al. also discusses inkjet-printed capacitors based on silver electrodes and high-k BaTiO3 dielectric formulated as a resin ink. However, they do not state the capacitance. [7] Li et al. report about all-inkjet-printed capacitors for wearable applications on kapton films. [13] In this work, the UV curable polymer SU-8 which is well known in the electronic industries, was employed as the dielectric. In contrast to the solvent-based dielectrics, UV curable materials are very promising for roll-to-roll processing as they allow curing within seconds or even milliseconds. Li et al. obtained a capacitance of about 48.5 pF for an active area of 19.63 mm². [13]

**METHODOLOGY**

*Layout and Architecture*

For printing the capacitors, digital patterns were created. The generated digital models are based on the MIM architecture shown in fig. 1 (a).
The actual size of the patterns can be seen in fig. 1 (b). The pattern itself explains the orientation of the different intended layers responsible to fabricate a capacitor e.g. the dark grey colored rectangle shows the bottom electrode ($5 \times 8 \text{ mm}^2$), the black colored next pattern is the dielectric layer ($5 \times 5 \text{ mm}^2$), and the light grey color of the last design is the top electrode ($3 \times 3 \text{ mm}^2$). Thus, effectively, the active area of the capacitors is expected to be the dimension of the top electrode which is $9 \text{ mm}^2$.

**Inkjet printing (functional materials)**

For fabricating the MIM capacitor, patterns following inks were used for the inkjet printing process. Both the top and the bottom electrodes are printed using SunTronic EMD5603 (“silver ink”) from SunChemicals, having 23 w/v % silver content dispersed in ethandiol and ethanol. The dielectric layer was printed with the UV curable ink Hyperion Pro Wet Black (“dielectric ink”) from Tritron GmbH, having the following contents: 1,6-hexanediol diacrylate (30 - 40 %), trimethylolpropane triacrylate (20 - 30 %), vinyl caprolactam (5 - 10 %), alkylphenone (5 - 10 %), acrylate ester (< 0.5 %). The ink involves 99% polymer content. These inks were printed on microscope glass slide substrates purchased from VWR. These glass slides were 1.3 mm thick with a dimension of 76 x 26 mm$^2$. Inkjet printing was performed with the Dimatix Materials Printer DMP 2831 from Fujifilm Dimatix, using 10 pL nominal droplet volume. The waveforms (with a frequency of 5 kHz) for ejecting the droplets can be seen in the fig. 2 (a) and (b).

**Workflow methodologies**

The curing of the printed wet dielectric layers was performed using the Dymax BlueWave 75 UV light spot lamp, and the pre-treatment on the silver layers
was done using an Arcotec CG 061 corona discharge unit. Preliminary tests were done by printing droplets of UV ink onto the silver layer which is untreated and pretreated with corona (at 0.4 kW). The design of the printing experiments can be seen in fig. 3, where the curing workflows for the dielectric layer are explained in detail. The first curing workflow is termed as the "Conventional curing" process because this kind of process is usually applied in the commercial roll-to-roll UV inkjet systems. Here the inkjet printing of the dielectric is done completely, followed by curing for 17 s at an exposure distance of 4 cm from the substrate. Next curing workflow is termed as "Corona + Printing + Conventional curing", here the bottom electrode is fabricated, and then corona pre-treatment is done at 0.4 kW to increase the surface energy of the lower electrode. The intention is to enhance the spreading of the succeeding dielectric layer. After this, curing is followed with the same methodology (UV curing of 17 s at an exposure distance of 4 cm from the substrate). Inkjet printing process, in general, can be defined as a line by line deposition process. Each line is cured directly after their deposition before the printhead starts to deposit the next lines aiming to complete the rectangle. The UV curing conditions are the same as before. The explained curing workflow is defined as "Printing + Intermediate curing." Next workflow of curing is very similar to "Printing + Intermediate", except that the curing is done with a 0.1 s short UV pulse (lower intensity). The intention is not to cure the printed lines completely but to offer partial curing at the surface interface or the boundaries of the inkjet-printed patterns resulting in a pinning. Once the printing and the in-line partial curing is finished, a final long UV pulse (exposure time duration of 17 s, at a distance of 4 cm) is provided to the dielectric layer to cure it completely. This curing workflow is called as "Printing + Pinning + Conventional curing." The last curing workflow is the same as before, except that corona pre-treatment (at 0.4 kW) is also involved in the printing process. The workflow is hence termed as "Corona + Printing + Pinning + Conventional curing".

The electrical characterization was done using the Agilent LCR meter supported by the Manual probe system PM5 (Süss Microtec). Initially, the capacitors were checked for the short circuits with a multimeter. Afterwords, the capacitance for the devices was measured at a frequency of 50 kHz.

The inkjet-printed dielectric layer's morphological and topographical characteristics were evaluated using a Leica DM4000 light microscope and a Veeco Dektak 150 surface profilometer. The Scanning Electron Microscope (SEM) FEI Nova NanoSEM 200 equipped with an Auriga focused ion beam (FIB) system was employed for cross-sectional images showing the microstructure.

**RESULTS AND DISCUSSION**

The inkjet-printed silver layers were analyzed. For this purpose, microscopic images and surface profiles were made. The microscopic images in fig. 4 (a) & (b) show that during the process of the corona pre-treatment for the silver electrode layer, some irregularities are also introduced to the layer. Fig 4. (c) shows the surface profile of the same silver layer when it is untreated and once when it is
pre-treated with corona. In general, the average thickness of the printed silver layer was found to be around 250 ± 50 nm. Fig. 4 (d) shows a cross-sectional image of the printed and sintered bottom silver layer without corona treatment. FIB technology with a gallium ion source was applied to remove silver partially to obtain a cross-section. The printed silver layer was coated with a layer of platinum of about 100 nm. The image shows the microstructure of the silver layer which is a result of sintering time and sintering duration. [10] The sheet resistance of the silver was found to be 1.52 ± 0.03 Ω/□. The roughness of the silver layer is found to be extremely high for the corona treatment, ranging from 70 - 80 nm (peak to valley). The roughness of the layer is found to be extremely high for the corona treatment, ranging from 70 - 80 nm (peak to valley). The reason that the layer shows high roughness is because of the process of the corona treatment. The process involves surface treatment via the usage of high voltage and also the production of material removal from the layer. The layer is observed to be thinner when compared to the untreated silver layer.

Furthermore, as a preliminary result, inkjet-printed dielectric ink droplets on a silver layer were analyzed. In fig. 5, microscopic images of the droplets can be seen when it is deposited on an untreated silver layer and when the same is filed on a pre-treated one. It is seen clearly that the corona pre-treatment works efficiently. The calculated average diameter of an inkjet-printed dielectric ink droplet over an untreated silver layer was found to be 148 ± 14 µm. Whereas for a corona pre-treated silver layer it was found to be 173 ± 11 µm. The circumferential spreading of the dielectric ink droplet at the edges of untreated silver was found to be approximately 12 µm which is exactly half the value of pre-treated silver layer which is about 24 µm. It can also be seen that the layer at the circumference is rather thinner than at the middle part of the printed droplet.
Fig. 5. Microscopic images of single inkjet-printed wet dielectric droplets on (a) untreated, and (b) corona treated silver layers.

Fig. 6 shows the microscopic pictures of the inkjet-printed dielectric layers. The images are in accordance to the different curing workflows which were discussed in the previous section (Fig. 3). Fig. 6 (a) shows the cured dielectric layer corresponding to “Conventional curing” workflow. The layer was found to be uniformly distributed. Fig. 6 (b) shows the cured dielectric layer corresponding to “Corona + Printing + Conventional curing” workflow. The edges of the black dielectric layer were seen to be a bit expanded due to the corona pre-treatment, but the effect is minimal. Fig. 6 (c) shows the microscopic image of the cured dielectric layer processed with “Printing + Intermediate curing” workflow. Throughout the printed layer, the line like behavior can be seen easily. This is due to the complete curing process of the individual deposited lines, while printing is carried out. Fig. 6 (d) and (e) below show the microscopic images of the cured layers when they are processed with “Printing + Pinning + Conventional curing”, and “Corona + Printing + Pinning + Conventional curing” respectively. Both layers look the same, but the line like pattern on the top surface of the cured layer is still visible. When the line pattern is compared to Fig. 6 (c), it can be stated that the surface obtained by the pinning is much more smooth and more homogenous. This homogeneity arises from the workflow of the step by step UV curing process itself, which consists of the low-intensity short UV pulses. The exterior surface part of the layer gets pinned during printing and the complete curing is performed for 100% hardening after the printing is finished.

Surface profiles were taken to analyze the morphology and roughness of the printed and differently cured dielectric layers. Each time, ten surface scan measurements were performed across the printing direction. The average of the individual scans (across print direction) is shown in fig. 7, which describes the layer profile on the curing workflows. Using the same dielectric ink and the same set of constant deposition parameters, the surface profile of the cured layers are different from one another. The average roughness $R_{AV}$ of the printed dielectric layers were measured using Dektak profilometer regarding the maximum peak to the highest valley with regards to a surface scanned at the center of the printed dielectric layer. The measured values are shown in Table I.
### TABLE I

<table>
<thead>
<tr>
<th>Curing Workflow</th>
<th>( R_{AV} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Conventional”</td>
<td>100</td>
</tr>
<tr>
<td>“Corona + Conventional”</td>
<td>200</td>
</tr>
<tr>
<td>“Printing + Intermediate”</td>
<td>1000</td>
</tr>
<tr>
<td>“Printing + Pinning + Conventional”</td>
<td>100</td>
</tr>
<tr>
<td>“Corona + Printing + Pinning + Conventional”</td>
<td>150</td>
</tr>
</tbody>
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It can be clearly seen, that the “Conventional curing” at the end of the printing process as well as the “Printing + Pinning + Conventional curing” workflows both result in the lowest \( R_{AV} \) of about 100 nm compared to the other curing workflows. A previous corona treatment of the silver layer increases the \( R_{AV} \) values slightly to 200 nm for the “Corona + Conventional curing” workflow and 150 nm for the “Corona + Printing + Pinning + Conventional curing” workflow. Highest \( R_{AV} \) values are not applicable for the “Printing + Intermediate” workflow. Here each line was cured during printing, which results in a visible line structure (Fig. 6 c) and therefore a typical hill and valley profile, which causes this high roughness.

In a case of the first curing approach (“Conventional curing”), the thickness of the layer was found to be 7.9 ± 0.3 µm. The second curing approach (“Corona + Normal curing”) gives a higher layer thickness of 8.8 ± 0.7 µm. The reason for this effect can be from the usage of the corona pre-treatment itself. The phenomenon of corona can have an intensive effect at the exterior part of the printed layer and can stretch the layer at those parts even though the layer at the center remains in a contraction mode. Similar effects were seen in fig 5. The shape of the surface profile is the same when both the first and second curing workflows are compared. For both methods, one high peak is always formed on one side of the layer, rising for the purpose without corona pre-treatment up to 12 µm and with corona pre-treatment up to 10.8 µm. The reason for the high peaks can be due to the printing process and the tendency of the ink to flow back towards the initial print edge for the intended square pattern. When the third curing process (“Printing + Intermediate curing”) is considered, the shape of the surface profile is entirely different.

The layer is observed to have a lot of iterative zig-zag morphology with very high peaks. The peaks arise from the quick curing procedure just after the deposition of the inkjet-printed lines. The average thickness of the layer was found to be 6.7 ± 0.8 µm, which is less than the first and second curing procedures. When the fourth (“Printing + Pinning + Conventional curing”) and the fifth (“Corona+ Printing + Pinning + Conventional curing”) curing is considered, the surface profiles can be found to be much smoother when compared to the third curing workflow. The layers do not show any tendency of high and low peaks and this leads to higher roughness. The profile of the layer is also very uniform and does not show the high peak on one side of the printed layer as it was discussed for the “Conventional curing” and the “Corona +
Conventional curing” workflows. After measurement of the surface profiles, the silver layer was printed on all the stacks (consisting of a silver bottom electrode and dielectric layer) to complete the capacitors. Capacitance was measured taking into account six samples for each workflow methodology for the dielectric layer and hence for the capacitor. As expected, it was found that the capacitance is inversely proportional to the layer thickness, based on equation (1).

Fig. 8. Graph showing the dependence of layer thickness (LT) achieved by the various curing methodologies and the corresponding obtained capacitance (C) and dielectric material permittivity (“Material’s Processing Factor” MPF)

Fig. 8 shows the dependence of the measured average dielectric layer thickness (LT) to the determined capacitance (C), as well as the calculated dielectric material permittivity. The best-obtained capacitance among all the differently cured dielectric layers for the UV based capacitor was found to be achieved by the third workflow (“Printing + Intermediate curing”), with a value of 0.5 ± 0.01 nF/cm². Next, the lowest capacitance value measured was 0.37 ± 0.01 nF/cm² for the second workflow (“Corona + Conventional curing”). In general, the average capacitance obtained over the range of the different curing workflows was found to be around 0.43 nF/cm².

In addition to the measurement of the capacitance, the dielectric material permittivity was also calculated. The calculation of the dielectric material permittivity is done using reverse calculation from the equation (1) mentioned in the introduction. In theory, it is believed that the dielectric material permittivity of the material is always constant. The UV material ink used here has 2 phases, the first one is the monomer phase and the next is the process of hardening the polymer phase. On the other hand, it is also expected that when we perform inkjet printing of this ink as the dielectric layer for the capacitors, neglecting the pre/post treatment methods, the capacitance should always be the same. In fig. 6 and 7, it is seen that due to the difference in the pre- and post-treatment workflows, the morphology of the fabricated dielectric layers can also change proportionally. This variation in the morphology of the dielectric layer directly affects the capacitance and hence the dielectric material permittivity becomes a “Material's Processing Factor” (MPF). The constant of the dielectric ink material for an inkjet printing fabrication process changes, giving rise to the appropriate standard deviation for the employed pre- and post-treatment workflow. In fig. 8 such an illustration is provided. It is seen that with the varying capacitance, the MPF also fluctuates. The MPF varies between the range of 4.1 ± 0.4 to 4.6 ± 0.3. The highest and the lowest MPF can be found for the fifth and second workflows which are “Corona+ Printing + Pinning + Conventional curing” and “Corona + Conventional curing” respectively. When all the MPFs are considered regarding the different workflow methodologies, then the average dielectric material MPF can result to approximately 4.3 ± 0.3.

The fabrication yield of the inkjet-printed capacitors was calculated considering six capacitors for each workflow. Out of these six capacitors, the number of working and non-working capacitors was taken into account depending on the primary capacitor property to isolate the top and bottom electrodes.

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Fig. 9 shows the fabrication yield for the all inkjet-printed UV capacitors, considering the 5 different workflows. It was found that the third and fifth workflow gave the maximum number of shorts with a fabrication yield of only 50%. The reason for this maximum amount of short circuits for the capacitors comes from the morphological aspects. Considering the surface profiles mentioned in fig. 7 and fig. 4 (c), we can see that third workflow gave the maximum amount of the different peaks and also valleys. It is furthermore expected that when there is a deep valley, there can also be a possibility of the valley to extend towards the bottom electrode. Furthermore, when the top electrode is printed, the ink can proportionally penetrate through the deep valley and then to the lower electrode. This can lead to the short circuits. It is also observed that the fabrication yield for the capacitors manufactured with the fifth method is the least. The reason can be explained by the process of corona pre-treatment itself. The pre-treatment process offers extra spreading of the dielectric ink that is deposited and in parallel pinned/cured step by step. This process can lead to relatively thinner printed dielectric layers (in a controlled manner). And since the partial curing is done immediately, there can be chances that the written lines for every print swath can lead to a small defect. Eventually, this weakness can lead to the electrical short circuit between the top and the bottom electrode.

CONCLUSION

We have demonstrated the fabrication of the all-inkjet-printed capacitor with a UV curable dielectric with all the involved fabrication and workflow steps. The focus was set on the curing processes for the dielectric layer. The best curing workflow to achieve the highest capacitance as well as the maximum fabrication yield is the fourth method which is "Printing + Pinning + Conventional curing". Various UV curing workflows have been discussed in this research work so as to control the process of curing and hence the layer formation or morphology of the dielectric layer. Influence of the inkjet printing process and the furthermore step of curing can have a direct impact towards the electrical and the physical property of the printed electronic device. Therefore, the prime importance for the fabrication of these printed electronic devices is the control over the morphology of the deposited layers and layer dependence towards each other. Inkjet printing technology has its attributes which can lead to a process and material dependent factors for the functionality of printed electronic devices.

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