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Nano-ink Drops' Behavior on the Polymeric Substrates' Surfaces

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Peter Lukács[1*], Alena Pietriková[1]

RESEARCH ARTICLE

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Abstract
The aim of this paper is analysis of the nano-ink behavior onto the polymeric substrates' surfaces. For this reason, three types of commonly used polymeric substrates for inkjet printing technology, polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and polyimide (PI) were analyzed. The impact of the surfaces' temperature on the ink spreading was mainly analyzed by using the microscopic methods. The higher temperature of substrate causes the fast evaporation process of the ink onto the substrates surface as well as causes the viscosity decreasing of the nano-ink. For this purpose, 2 silver based nano-inks were deposited by inkjet printer Jetlab 4xl-A with orifice diameter 70 µm. The main benefit of this paper lays in the optimizing of the spreading and coffee ring effect of several silver based nano-inks through the surface temperature changes and investigation of the deposited structures' shapes after the sintering.

Keywords
inkjet printing, nano-inks, polymeric surfaces, ink spreading, coffee ring effect

[1] Department of Technologies in Electronics,
Faculty of Electrical Engineering and Informatics,
Technical University of Kosice,
Letna 9, 042 00 Kosice, Slovakia
[*] Corresponding author, e-mail: peter.lukacs@tuke.sk

1 Introduction

The inkjet printing technology, as a relatively new technology in the field of electronics brings a lot of possibilities to deposition of special nano-inks onto the polymeric substrates with high accuracy. The application range of described technology is an ever wider, especially in the cases, where the precision of printing and the high accuracy plays a key role. On the other hand, the advantages of this technology are related to the challenges, which must be taken into consideration during the deposition process, such as surface properties of polymeric substrates, technological aspects as well as the parameters of nano-inks. All of these challenges have the immediate impact on the final parameters of printed structure. For the reason of very low thickness of printed structure (less than 1 µm), the surface roughness Ra of polymeric substrates are very important not just for achieving the good adhesion between the printed layer and substrate but also for the ink spreading on the substrate's surface [1, 7-10].

The deposition process of nano-ink onto the flexible substrates with high precision, creation the suitable adhesion mechanism and recommended curing conditions are influenced by many technological steps, which are closely related. Uncontrolled process of the ink spreading on the surfaces causes the formation of the coffee ring effect, as well as the inhomogeneous structure. The compatibility of the concrete nano-ink, polymeric substrate, nozzle diameter as well as the inkjet printer requires the special approach for finding the best technological aspects for creation the final structures with high quality. The optimization process of the drops' deposition is major challenge in this technology solved worldwide [1-3, 8, 9].

The homogeneity maintaining of the created structures by inkjet printing technology is necessary for achieving the strictly defined properties of the structures. It is generally known, that the higher temperature causes the coffee ring effect creation, especially in the case of inkjet printing technology. One of the methods to resolve this challenge is control of the ink spreading on the substrate surfaces via temperature setting of the substrate [3, 5, 9, 11].

The morphology of the printed conductive layers is dependent upon a number of printing conditions which include drop spacing, print width and substrate temperature [3]. If the specific surface area at every point of evaporating droplets is different, the height reduced by the evaporation flux is non-uniform and the evaporated volume in the central area is smaller than the volume in the edge area. When the droplet has a pinned three phase contact line (TCL) the excess solvent lost at the edge is replenished by solvent in the center, leading to a radial capillary flow. The capillary flow carries the solutes in evaporating droplet towards the pinned TCL, thus the ring-like morphology is formed [4].

Droplet impact and spreading affect the minimum feature size that can be achieved. Droplet deposition can be divided into 2 stages. The first stage of droplet deposition is an impact driven stage of less than 1 ms duration, where the kinetic energy of the impact is partially dissipated by viscous forces. The residue of this energy is converted into surface energy, which spreads the droplet to a diameter determined by the relative surface energy between the ink and the substrate in the second stage of the deposition process [5].

The ink's resistance to spreading can be characterized by the Ohnesorge number O_h, which describes the droplet formation and it is the ratio of the viscous forces to the surface tension and inertial forces. A high number indicates that resistive force is due to viscosity, whereas for a low number it is due to inertial forces [5]:

$$O_h = \eta / (\rho L \sigma)^{1/2} = W_e^{1/2} / R_e \quad (1)$$

where,
ρ is the density,
η is the viscosity,
σ is the surface tension,
L is the nozzle diameter,
W_e is the Weber number and
R_e is the Reynolds number.

2 Experimental

The investigation of the impact of surface properties on the nano-ink behaviour was realized by using the inkjet printer MicroFab® Jetlab 4xl-A with orifice diameter of 70 μm.

Two kinds silver based nano-inks were used from two different manufacturers listed in the Table 1.

The surfaces of the used polymeric substrates polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and polyimide (PI) were cleaned by the isopropyl alcohol, which has the proved negligible impact onto the surface properties [1].

For the reason of detailed analysis of the different surfaces' properties impact on to the ink behavior after the deposition process, the special test pattern was designed. As it can be seen in the Fig. 1, the designed test pattern is divided into the three parts. The part A analyzes the impact of the nano-inks drop onto the substrates surfaces, the ink spreading, dot diameter and the shape of the dot. The part B is designed for testing of the printing precision. This part consists of the lines with different dimension and space, as well as of the crossing lines which will detect the shortcomings of the deposition process. The part C of the pattern is used for the investigation of the adhesion mechanism between silver layer and the substrate.

Table 1 Selected specifications of used silver based nano-inks

Silver based nano-inks	JP-6n	UTDAgIJ
Manufacturer	Amepox Mictroelectronics, Ltd.	UT Dots, Inc.
Percentage of silver [%]	40-60	25-60
Viscosity [mPas]	7.5-10.5	1-30
Particle size in diameter [nm]	3-7	10
Electrical resistivity [Ω.cm]	$(4-6)\times10^{-6}$	$(3-10)\times10^{-6}$
Recommended sintering conditions	220-230°C 60 min	120-300°C

The designed test pattern was printed on to the three polymeric substrates (PI, PET and PEN) while the temperature increased from the room temperature up to 100°C with the step of 5°C. The applied sintering conditions are listed in the Table 2.

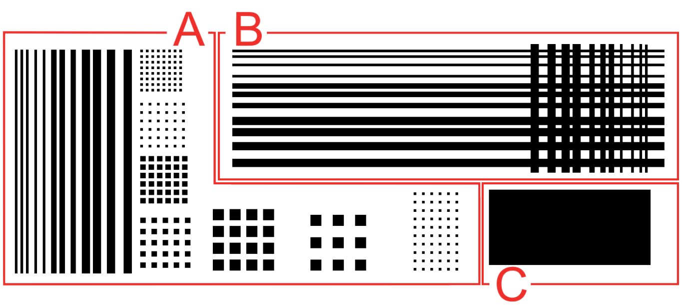

Fig. 1 Test pattern.

Table 2 Applied sintering conditions

Substrates / Ink	JP-6n	UTDAgIJ
PI DuPont™ Kapton® HN 200	220°C/60 min	220°C/60 min
PET Mylar® A FI	190C°/60 min	140°C/90 min
PEN Teonex® Q 51	190°C/60 min	150°C/90 min

The deposited test patterns on the 3 types of polymeric substrates (PI, PET and PEN) by silver based nano-inks were analyzed by 3D optical profiler Sensofar S Neox for the reason of detailed investigation of the drops' shapes dependence on the substrates temperature.

3 Results

This paper analyzes the silver based nano-inks drops quality after the impact onto the polymeric substrates surfaces by changing of the substrates temperature during the deposition process. The achieved results show the strong dependence of the dots shape on the substrates temperatures. The detailed results for two kinds of silver based nano-inks on three types of polymeric substrates are described below.

3.1 PET Substrate Mylar® A

PET substrate Mylar® A offers the cheaper adequate substitute for expensive PI substrate with surface roughness R_a 0.046 μm [1].

In the Fig. 2 is shown the required shape of the dot deposited by Amepox JP-6n silver based nano-ink on the PET substrate Mylar® A deposited at 70°C.

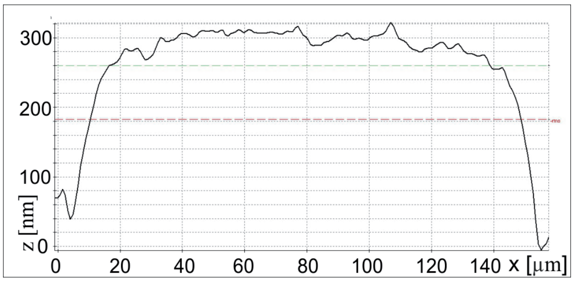

Fig. 2 Cross section of the profile of Ag based dot Amepox JP-6n on the PET Mylar® A substrate deposited at 70°C.

If the temperature of substrate during the deposition process increased up to 80°C, the shape of dot is formed to the coffee ring as it is shown in the Fig. 3. In the Fig. 4 is shown the typical example of the coffee ring effect on the PET substrate Mylar® A caused by the substrate temperature higher than 100°C.

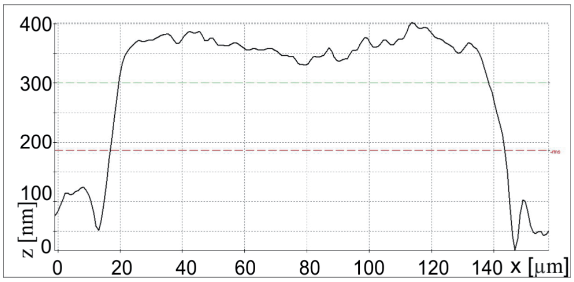

Fig. 3 Cross section of the profile of Ag based dot Amepox JP-6n on the PET Mylar® A substrate deposited at 80°C.

Very similar results were achieved in the case of the silver based nano-ink UTDAgIJ. The optimal temperature where the coffee ring effect is not occurring is about 70°C. The temperature higher than 70°C causes the strong coffee ring effect, which has a significant impact on the homogeneity of the printed structure.

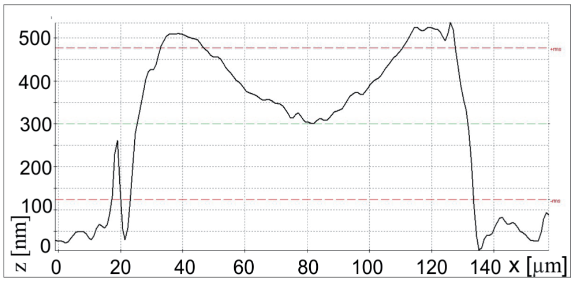

Fig. 4 Cross section of the profile of Ag based dot Amepox JP-6n on the PET Mylar® A substrate deposited at 100°C.

3.2 PI substrate Kapton® HN 200

Polymeric PI substrate Kapton® HN is one of the most commonly used polymeric substrate for inkjet printing technology for the reason of high temperate resistance as well as stable mechanical properties. The surface roughness R_a of described PI substrate is 0.044 μm [1].

The ink spreading on the PI substrate Kapton® HN is very similar to the PET substrate due to the same value of the roughness. The nano-ink Amepox JP-6n had the homogenous structure up to temperature 70°C. Above this temperature there is the significant impact of the fast solvent evaporation on the drop's shape which causes the coffee ring effect. This causes the increases of the dot's height to the detriment of the dot's width which decreases.

In the case of the nano-ink UTDAgIJ, the limit temperature to the coffee ring effect creation is 60°C. The shape of the dot on the substrate is rapidly changed where the edge of the dot grows whereas in the center of the drop is going on the fast solvent evaporation and the drop dries above the temperature 60°C.

3.3 PEN substrate Teonex® Q 51

PEN substrate Teonex® Q 51 is characterized by higher temperature resistance, than PET Mylar® A and therefore it is often used for inkjet printing technology. The surface roughness R_a of PEN Teonex® Q 51 is 0.020 μm [1]. This is the reason of the wider dots under the deposition process. The lower surface roughness allows the significant ink spreading on the surface of the polymeric substrate. On the other hand, the lower surface roughness results in the worse adhesion mechanism between the deposited layer and the substrate. The optimal temperature value for achieving the homogenous structure with strictly defined shape for the nano-ink Amepox JP-6n on the substrate PEN Teonex® Q51 is 70°C. The temperature higher than 70°C causes the coffee rings, which are not desirable. The optimal substrate temperature for nano-ink UTDAgIJ is 50°C, where the homogeneity of the deposited structure is maintained. Temperature higher than 50°C causes the coffee ring effect.

In the Fig. 5 is shown the suitable shape of the dot and in the Fig. 6 is shown the typical example of the coffee ring effect of the dot deposited onto the PEN Teonex® Q 51.

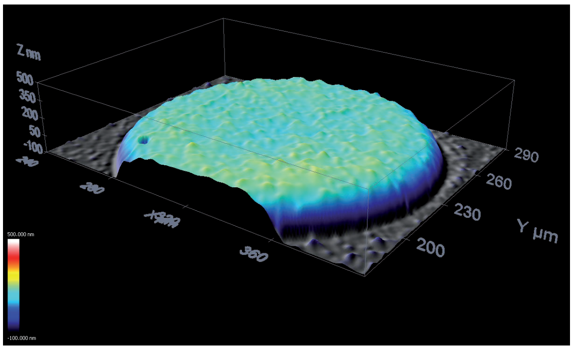

Fig. 5 3D profile of Ag based dot Amepox JP-6n on the PEN Teonex® Q 51 substrate deposited at 80°C.

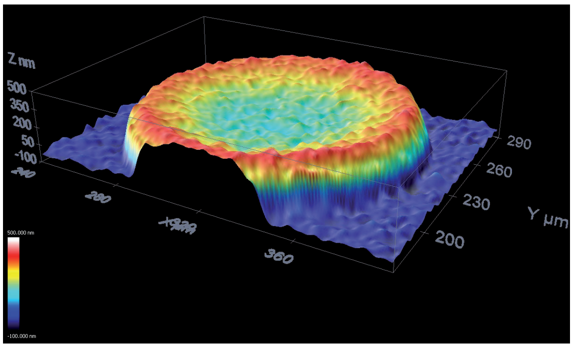

Fig. 6 3D profile of Ag based dot UTDots UTDAgIJ on the PEN Teonex® Q 51 substrate deposited at 100°C.

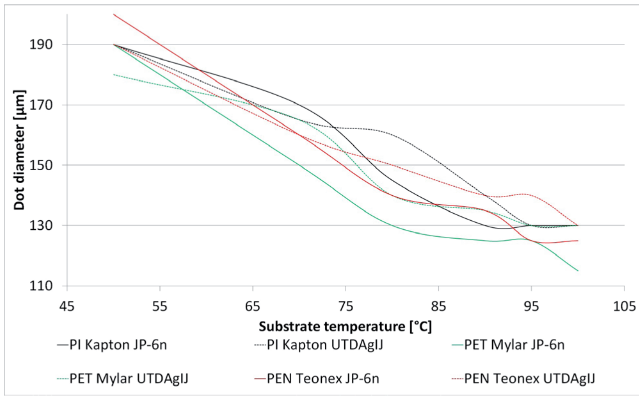

Fig. 7 Influence of the substrate temperature to the dot diameter.

In the Table 3 the summarization of the optimal temperatures for the achieving the homogenous structure of the deposited layer are presented for two kinds of silver based nano-inks and three polymeric flexible substrates.

Table 3 The optimal temperatures for achieving the homogenous structure

Substrates / Ink	JP-6n	UTDAgIJ
PI DuPont™ Kapton® HN 200	70°C	60°C
PET Mylar® A FI	70C°	70°C
PEN Teonex® Q 51	70°C	50°C

It is clear from the detailed investigation of the drops' behavior that the significant impact on the drop diameter and the ink spreading has the substrates' temperature. On the other hand the surface roughness Ra does not has the considerable impact on the drops' behavior.

The Figure 7 presents the influence of the substrate temperature to the dot diameter of the whole investigated polymeric substrates.

4 Discussion

The aim of this paper is based on the need of the analysis of the nano-inks' behavior during and immediately after the deposition process. For the reason of various parameters and used solvents in the nano-inks, the ink spreading on the substrates' surfaces can be absolutely different. This fact incites the necessity of finding the optimal deposition parameters for every nano-ink and polymeric substrate. It is impossible to create the structure with high precision without determination of the parameters, which has the significant impact on the drops quality. One of these parameter is the substrate temperature during the deposition process, which has been easily changed.

The results shown in this paper prove the strong dependence of the substrates temperature on the drops behavior also determines the temperature limit for two kinds of silver based nano-inks and three polymeric substrates where the drops have the homogeneous structures.

The prediction of the dot's behavior on the substrates surfaces, as well as the ink spreading and final dot diameter is very difficult for the reason of many parameters of the nano-inks, substrates and technology. In addition the nano-ink parameters given by manufacturers on the data sheets are often inaccurate or are given in the very wide range. The percentage of silver of the investigated nano-inks is up to 60 % which has the certain effect on the inks viscosity. This parameter is different in the both of analyzed nano-inks. In the case of nano-ink JP-6n it is 7.5–10.5 mPas, whereas for UTDAgIJ it is in the range of 1 up to 30 mPas. This may have a considerable impact on the ink spreading on the substrates surface at low temperatures. If the substrate temperature rises up the drop height reduced by the evaporation flux is non-uniform and the evaporated volume in the central area is smaller than the volume in the edge area. The result of this phenomena is the coffee ring effect creation which is the undesirable effect.

The easiest method for elimination of the coffee ring effect and achieving the homogeneous structure is the temperature control of the substrate during the deposition process of the nano-ink. It is very important to take into the consideration that every type of nano-ink and substrate may have the different temperature limit for creation of the coffee rings. The next substantial result lays in the fact that the surface roughness Ra of the analyzed polymeric substrates does not have the significant impact on to the drop spreading or the coffee ring effect creation. On the other hand the surface roughness Ra has the considerable impact on to the adhesion mechanism between the deposited silver layer and the substrates' surfaces.

5 Conclusion

In this paper the nano-ink drops behavior was analyzed for three commonly used flexible polymeric substrates (PI, PET and PEN) by using of two kinds silver based nano-inks at different substrates' temperatures.

The achieved results prove the theory of the coffee ring effect creation caused by the high temperature in inkjet printing technology which adversely affects the homogeneity of the deposited structure. With regard to the achieved results it can be told the substrate temperature higher than 70°C causes the fast evaporation process of the solvents contained in the nano-inks in all cases of the investigated substrates for the nano-ink JP-6n. For the nano-ink UTDAgIJ the temperature limit is different for every analyzed polymeric substrate. The lowest temperature (50°C) is in the case of PEN substrate Teonex® while the highest temperature (70°C) is for the PET foil Mylar®. The optimal temperature for the PI foil Kapton® is about 60°C. It is necessary to consider the fact that the higher substrate temperature allows to print the more precise structures nevertheless the homogeneity throughout the whole volume is not maintained.

The elevated substrate temperature has a directly impact on the drops diameter after the deposition process. For this reason there is the necessity to choose the sufficient compromise between the drops shape and the drops diameter.

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