Conductivity and microstructure of inkjet printed nanoparticle silver layers processed with intense pulsed light (IPL) sintering on various polymeric substrates

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Abstract

Novel manufacturing methods for flexible, light weight and cost-efficient electronics have gained high interests in the recent years, especially the additive printing technologies are of major relevance. Here, the digital inkjet printing technology is an attractive printing method due to its additive, high precision and up-scalable deposition process. One of the key components of a printed electronic device, such as capacitor, transistor and sensor, is the conducting track. A major requirement is the device dependent electrical performance induced by an appropriate post treatment process. Traditional thermal sintering via an oven or hotplate requires on one hand long sintering times (up to minutes and hours) and on the other hand high sintering temperatures (above 150 °C - 300 °C), which are unsuitable for flexible polymeric foils with low glass transition or melting temperature. However, the novel method of intense pulsed light (IPL) sintering has great potential when it comes to the fabrication of functional layers on thin, flexible and temperature instable polymeric foils. In our research, the IPL sintering methodology is used to convert printed liquid films into solid and conducting metallic layers on various flexible polymeric substrates, like Polyethylene terephthalate (PET), Polyethylene naphthalate (PEN) and Polyimide (PI). Based on their glass transition temperature as well as applied energy densities the defect formation in the micrometer rang was analyzed. Furthermore, the electrical performance was measured and the conductivity calculated. It was found, that the substrate material property in terms of glass transition temperature and melting point have a prominent influence on the defect rate and the electrical performance.

Introduction

To convert printed liquid films into solid functional layers with the desired microstructure as well as electrical performance, a suitable post treatment methodology is required. Thereby, solvents and additives are evaporated, all organics are casted out and the metallic nanoparticle are merged together [1] [2]. Especially for the merging and melting together of the nanoparticles into a compact metallic microstructure, high temperatures have to be applied, which makes this process not suitable for thermal instable polymeric substrates like PET or PEN foils [1] [3] [4] [5] [2]. In order to achieve desired electrical performances even on ultrathin, flexible and stretchable substrates, which cannot withstand high temperature treatments, novel sintering methods are introduced. These technologies use e.g. laser [6], infrared (IR) radiation [7], microwaves [8] or intense pulsed light (IPL) [9] [10] to introduce the heat selectively inside the printed structures.

In the case of the usage of intense pulsed light, the sample is irradiated by high intense light flashes, which only get absorbed by the dark nanoparticles inside the printed film. [11] [12] Polymer foils are due to their transparency not or only minor affected by the light and hence not directly heated. [12] The process of photonic sintering is in the range of microseconds (µs) to milliseconds (ms), but in the case of multiple pulses also up to several seconds [13]. Even a drastic increase in temperature inside the printed metal layer only lasts for a few milliseconds or maximum a few seconds, which is theoretically too fast to affect the subjacent substrate. Nevertheless, this heat impact has to be taken into account at the border of the heated metal layer and the polymer substrate [10] and will be further discussed within this research.

Materials and Methods

The silver nanoparticle ink used in this work is Sicrys I50T-11 (pvnanocell). The various used polymeric foils and their glass transition temperature as well as melting point are summarized in the table 1 and table 2. All substrates were cleaned with ethanol and compressed air before printing. Printing was carried out with a Dimatix Materials Printer (DMP 2831 from Fujifilm Dimatix) with 10 pL printheads. The print pattern consists of squares with 5 x 5 mm^2 dimensions as well as various narrow lines of 5 mm length and 1-3 pixel in width. The patterns were analyzed based on electrical characteristics by means of sheet resistance measurements, visual characterization by a light microscope and a surface profile analysis with a Dektak. The printed samples were dried at 60 °C for 10 minutes. Flashing was carried out with the PulseForge 3200 from Novacentrix. This flash lamp is integrated in a hybrid R2R modular printing machine from 3D-Micromac AG, which enables the inline printing and sintering on industrial scale.

Additionally, a thermal sintering on a hotplate for the ink printed on a glass substrate was carried out as a reference.

Table 1: Overview on the substrates used in the thesis

Material	Product Name	Thickness [µm]
PET	Melinex® 401	50
PEN	Q65HA	50
PI	Kapton HN FI 16010	50

Table 2: Specification of the substrates and subsrtate materiasl given from the datasheet and literature

	melting temperature [°C]	Tg [°C]
PET	265 [14]	68 [16]
	258 (film) [15]	100 (film) [15]
PEN	269 [15]	155 (film) [15]
PI	None [15]	None [15]

Results and discussion

Electrical investigation

The conductivity of the thermal sintering and the IPL sintering is displayed in ***Figure 1*** and was calculated based on measurements of the sheet resistance and the layer thickness.

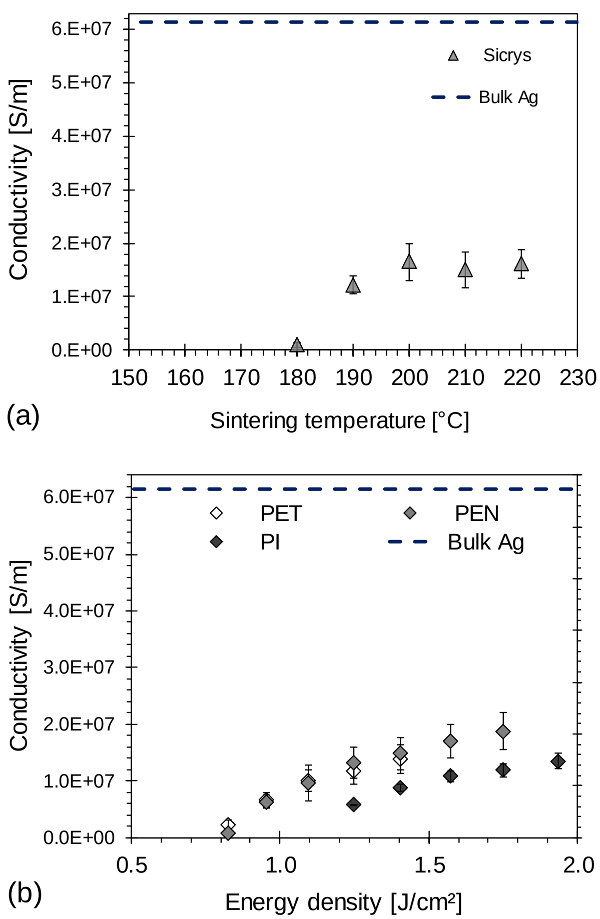

***Figure 1**. Comparison of the conductivity of the Sicrys silver ink on various substrates for: a) thermal sintering of samples printed on a glass substrate and sintered on a hotplate; b) IPL sintering on various polymeric flexible foils.*

The maximum percentage of the bulk silver conductivity achieved with thermal sintering is 27 % at 200 °C for 10 minutes. Increasing the temperature does not increase the conductivity further, it just fluctuates and remains static within the standard deviation. Knowing, that for the polymeric foils PEN and PET a temperature exceeding 160 °C destroys (by bending or melting) the substrate, but a minimum sintering temperature of 180 °C is required to achieve at least 2 % bulk silver conductivity, makes this ink not applicable for the usage of these low temperature stable polymeric foils with the traditional thermal sintering. However, the IPL sintering resulted in 23 % for the PET and 24 % for the PEN foil at 1.41 J/cm² as well as 13 % on the PI substrate at 1.94 J/cm². The results on the PET and PEN foils are comparable same, but exceeding the energy density of 1.41 J/cm² caused delamination and burning defects within the silver layers and especially on the PET foil no conductivity could be measured anymore. Although, raising the energy density on the PEN foil up to 1.75 J/cm² and achieving a slight further increase in the bulk silver conductivity was possible, the silver layer revealed major defects and is not applicable in printed electronic devices anymore. On the PI foil no defects in the silver layer could be identified up to 1.94 J/cm², but exceeding this energy density caused a slight bending of the PI foil, therefore the energy was not raised more. The comparable lower conductivity on the PI substrate can be explained by the higher thermal conductivity of the PI material, which leads to a faster heat conduction and a reduced sintering effect [17].

Optical investigation

In ***Figure 2*** microscopic images of the silver layers printed on the three foils are presented after IPL sintering with lower energy densities. It can be clearly seen, that the silver patterns do not show defects in the macroscopic range, such as delamination and flaking of. But as shown in the magnification of the edge small micro cracks appear already at an IPL energy density of 0.82 J/cm² for the samples printed on the PET and the PEN foil. These micro-cracks have a characteristic course, which runs around the complete square pattern at the interface of the silver layer and the substrate, means alongside the outline of the square. This can be seen by the black border around the printed and flashed squares from the ***Figure 2***a and ***Figure 2***b. The dark border is most demonstrative for the silver printed on the PET foil (***Figure 2***a), where the magnification also reveals a visible crack formation (***Figure 2***d). Besides the dark edge is noticeable for the PEN foil (***Figure 2***b), the magnification shows only very minor micro-cracks (***Figure 2***e) at the edge. On the contrary, for the samples printed and flashed on the PI foil no black border is visible in the macroscopic range (***Figure 2***c) and no cracks can be identified in the microscopic view (***Figure 2***f), despites a comparable high flashing energy density of 1.41 J/cm² was used.

After increasing the energy density, the characteristic black border and the associated crack at the silver-substrate interface are drastically intensified for the PET and the PEN substrate, as demonstrated in ***Figure 3***a and ***Figure 3***b, respectively. On both foils burning defects at the edges and corners appear in larger scale. Considering the microscopic scale, the previous small cracks enlarged to major cracks and it seems like the silver layer teared of in this area. On the PI foil (***Figure 3***c and ***Figure 3***f) again no crack or any conspicuity of burning defect can be recognized.

With the optical investigation it can be summarized, that the thermal stability of the substrate, defined by the melting temperature as well as the Tg, influences the defect rate of the flashed silver samples. Especially in the microscopic range, the striking crack formation at the silver-substrate interface is higher the lower the Tg or melting temperature of the used substrate material is (referred to Table 2). However, the both polymeric foils PET and PEN have a similar melting temperature and therefor show a huge crack formation and burning defects after flashing with the high energy density of 1.41 J/cm². Only at the lower flashing energy density of 0.82 J/cm² the PEN foil, with its higher Tg, resulted in a minor crack formation as compared to the PET foil.

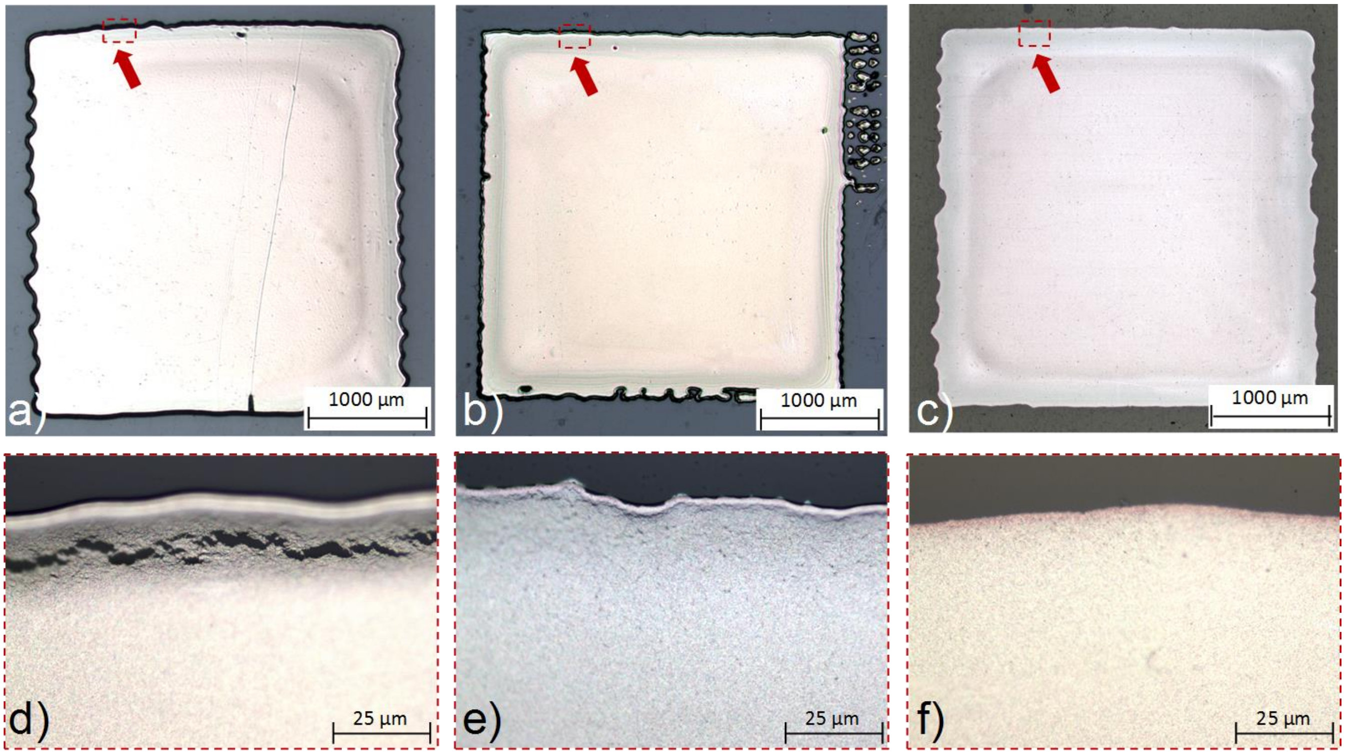

Figure 2*: Microscopic images of full squares and magnification at the edge, inkjet printed on the three polymeric substrates and IPL treated with various parameters: a) full square on PET at 0.82 J/cm²; b)) full square on PEN at 0.82 J/cm²; c) full square on PI at 1.41 J/cm²; d) edge of square on PET at 0.82 J/cm²; e) edge of square on PEN at 0.82 J/cm²; f) edge of square on PI at 1.41 J/cm²*

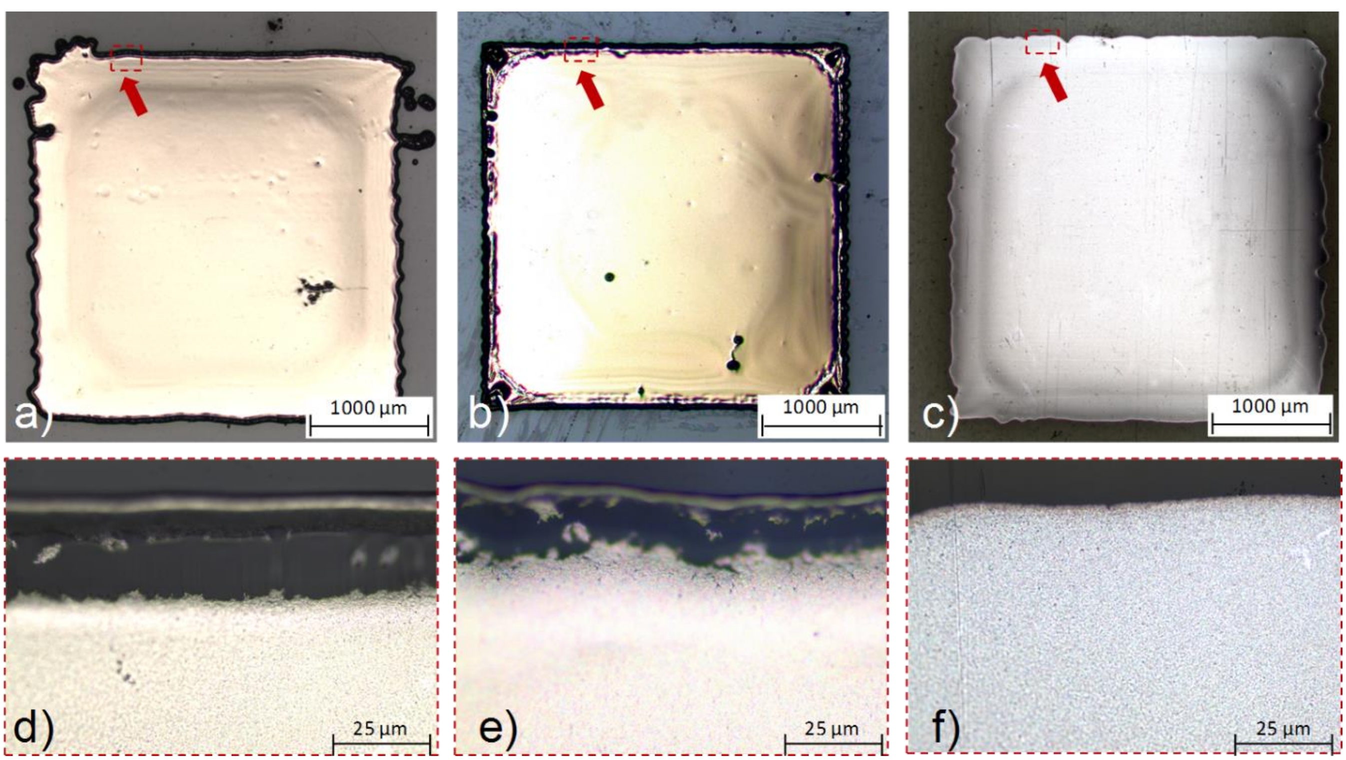

Figure 3*: Microscopic images of full squares and magnification at the edge, inkjet printed on the three polymeric substrates and IPL treated with various parameters: a) full square on PET at 1.41 J/cm²; b)) full square on PEN at 1.41 J/cm²; c) full square on PI at 1.94 J/cm²; d) edge of square on PET at 1.41 J/cm²; e) edge of square on PEN at 1.41 J/cm²; f) edge of square on PI at 1.94 J/cm².*

It can therefore be concluded, that polymeric foils with lower thermal stability result in damage inside the printed silver layer if the temperature within the layer exceeds their Tg or melting point during the IPL treatment. The PI foil has no defined Tg or melting temperature and therefor resulted in no defects in the silver or substrate.

Micro crack investigation

For a deeper understanding of the crack at the silver-substrate interface, a profile scan was carried out across the crack of the area marked (red square) from ***Figure 2*** and ***Figure 3***. The results are presented in the graphs in ***Figure 4***.

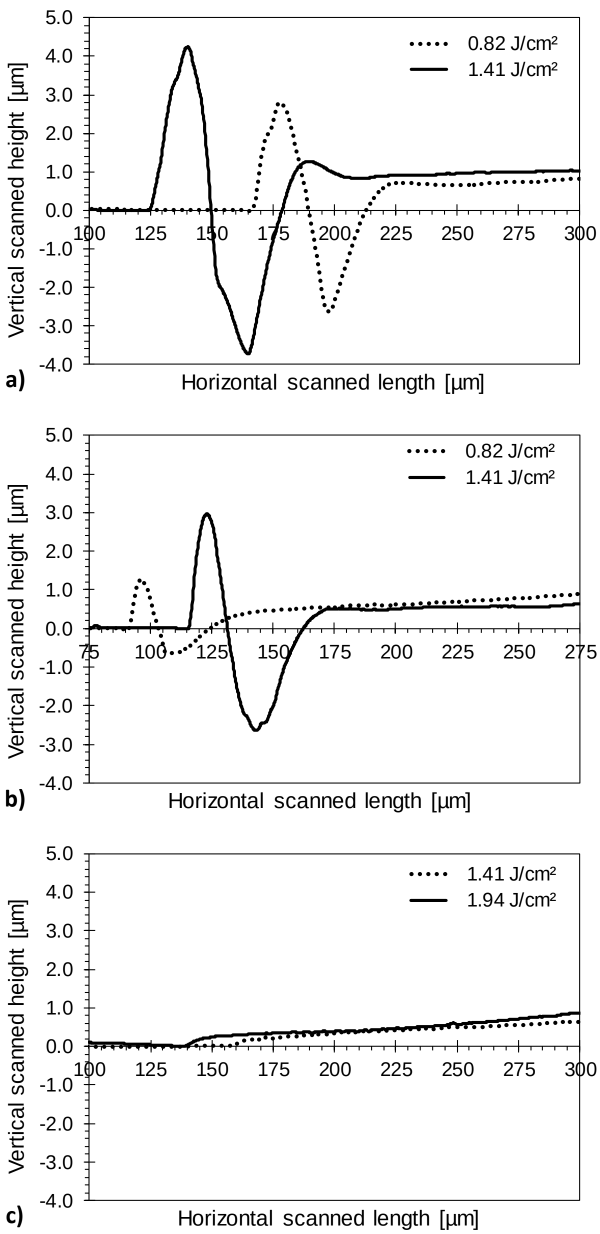

***Figure 4**: Surface profiles (Veeco Dektak) across the edge of the samples presented from figure 2 after IPL sintering with two various flashing energy densities: a) printed on PET; b) printed on PEN; c) printed on PI.*

The graphs present a hill and valley deformation at the edge of the silver layer printed on the PET and PEN substrate, recording a deformation ranging several µm high and into the respective foil. On the Example of the PET foil flashed with 0.82 J/cm² (***Figure 4***a), it can be observed, that the profile starts around the 0 µm level, which is the undeformed foil (leveled to 0), and proceeds towards a hill up to 3 µm after which it runs into a valley down to -3 µm. Then the profile continues at around 1 µm further across the silver layer. Superimposing the microscopic images and the respective profile it becomes clear, that the recoded hill represents the silver border and the valley must be the crack or teared of area.

These deformations might be caused by the heat impact from the silver layer and an arising stress within the polymeric foil at the border to the silver layer. Despites that the transparent substrate is not directly affected by the intense pulsed light, the heat development inside the silver layer is conducted through the silver and conducted into the substrate. This can lead to tension, especial at the border of the silver between heated substrate and non-heated substrate.

Furthermore, a higher energy density caused an increased hill and valley formation, which was also observable in the high crack and tearing off from ***Figure 3***a. Comparing the PET and PEN substrate, the hill and valley formation is much lower on the PEN substrate at 0.82 J/cm² and slightly lower at 1.41 J/cm². Here again the suggestion can be made, that the PEN has a higher Tg and therefore resulted in smaller deformation due to its higher thermal stability. As it can be seen from ***Figure 4***c, the heat stable PI foil does not show any deformation in its layer profile at both, lower and higher energy density, as it also showed no optical defects from ***Figure 2***f and ***Figure 3***f.

Conclusions

In this research a nanoparticle silver ink was inkjet printed onto three flexible polymeric foils with different thermal stabilities and Tg. Based on this, the impact of the intense pulsed light (IPL) sintering on the silver layers as well as the substrate was investigated. It was found, that at lower flashing energy density no defects on the silver layer and the substrate were cause by the IPL sintering in the macroscopic scale. However, the microscopic analysis revealed minor cracks at the silver border for the thermally less stable PET and PEN foils. This cracks enlarged after flashing with higher energy density and could be detected as a deformation within the silver layer as well as the substrate in the range of a few µm in depth. On the PI foil, no defects were caused in the macroscopic and microscopic range, even at higher energy densities.

Such cracks and deformations, even only in the µm range, need to be taken into account e.g. in multilayer stacks as well as their impact on the electrical performance of the single layer and the whole device.

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Author Biography

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