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Direct Printing of Conductive Metal Lines from Molten Solder Jets via StarJet Technology on Thin, Flexible Polymer Substrates

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Abstract

We present the direct printing of thin (linewidth of 70 µm) conductive lines from molten solder on thin, flexible substrates. The lines are generated via the so-called StarJet technology that enables the printing of micro jets from molten metal. In this work, metal lines are printed for the first time on flexible substrates, possibly enabling applications in the field of printed electronics. The printed lines are evaluated regarding their mechanical and electrical properties. To the knowledge of the authors, this is the first time that direct printing of a functional metallization, requiring no further treatment, on a flexible polymer substrate was demonstrated. The lines exhibit a low ohmic resistance and can endure shear forces of up to 3.5 N on polyethylene terephthalate (PET) substrates.

Introduction

The demand for electronics on thin, flexible substrates has grown significantly over the last few years as new applications such as wearable systems started to emerge [1]. Currently, inkjet printing has become one of the key technologies to bring highly-sophisticated electronics onto flexible substrates such as polymer foils [2]. The main focus of flexible electronics are focused on realizing different printed functionalities on flexible substrates such as RFID tags [3], bio-sensors [4], actuators [5], micro-heaters [6], organic solar cells [7], supercapacitors [8] and batteries [9]. In order to achieve electronic applications, stable, bendable, and highly conductive electrical wiring is the core component to deliver electrical power and signals to the electronic circuits. Although printing technologies such as inkjet and aerosol jet printing have enabled direct printing of excellent features from conductive materials such as silver and gold nanoparticle inks, the conductivity, stability, and the manufacturing cost of printed structures are still not fully meeting the industrial requirements. Key shortcomings are the rather low electrical conductivity of the printed metal lines and relatively low mechanical stability on the substrate, which requires protective coating/foil to avoid mechanical damages. Furthermore, a post-treatment such as thermal or photonic sintering is usually required to achieve the final functionality, which increases the complexity of the production process and limits the choice of substrates.

In contrast, the StarJet technology provides a direct and non-contact metal printing directly from molten metals under ambient conditions, which was invented and developed at IMTEK - University of Freiburg [10]. Therefore, no post-treatment is required and printed structures exhibit high aspect ratio of ~1:1 [11]. Compared to the state-of-art printing technique, no multi-layer printing is needed and it has lower total resistance. Furthermore, examples of electrically functional, direct metallization by StarJet technology were successfully demonstrated on silicon solar cells [11] and PCB boards [12].

In this contribution, direct solder line printing on flexible substrate via StarJet Technology is demonstrated for the first time. In contrast to state-of-the-art flexible electronic printing techniques, which consist of printing, drying and sintering, the metal (solder) is first molten in the printhead, and directly printed onto the flexible substrates. The molten solder cools rapidly after jetted from the nozzle. Due to the limited thermal capacity of the thin printed line, only the surface below the printed solder lines is partly melt and forms strong adhesion between printed solder lines and the substrate. Consequently, the printed solders lines show high flexibility, low resistance and high robustness on polymer substrates.

Experimental

StarJet Technology

The StarJet method provides a one-step, non-contact metallization from molten metal. It bases on a pneumatically driven printhead that features a heatable reservoir, containing the molten metal, and an interchangeable nozzle chip featuring a star-shaped orifice geometry. This geometry leads to a centering of droplets in the orifice due to capillary forces because of non-wetting contact angles of the molten metal on the nozzle chip material. Different printhead prototypes based on the StarJet method can be operated at temperatures above melting temperatures of metals such as solder [10] and aluminum alloys [13]. Thanks to the pneumatic actuation, no thermally limited piezoelectric actuators are required, which are widely used i.e. for inkjet printheads and depolarize above their Curie temperature. Therefore, a high operating temperature of up to 950 °C is possible with current experimental setups.

StarJet printheads feature two independent gas pressures. A constant rinse gas pressure establishes a flow through the star-shaped bypass channels that provides an inert gas shielding of printed molten metal. The so-called actuation gas pressure is used to apply pressure to the reservoir via a solenoid valve. By tuning the actuation and rinse gas pressures and the actuation time via the valve, three different jetting modes can be realized: Drop-on-Demand (DoD) mode [14], continuous mode [15] and Jet mode [11]. In this contribution, Jet mode is exclusively used to deposit thin and fine solder lines on PET foils.

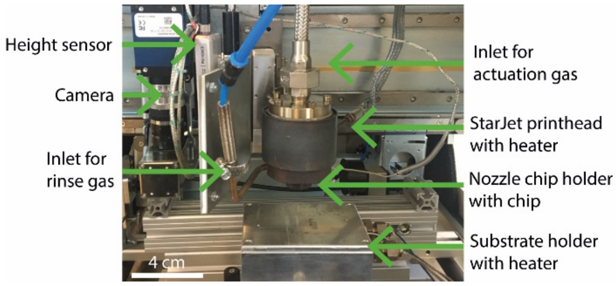

***Figure 1** Close-up photograph of StarJet-based printing system. The printhead is integrated in a Nordson Asymtek Spectrum II 910 machine and features the depicted components.*

Material and Methods

The solder Sn96Ag3Cu (Stannol, TSC305) was used as the raw material for printing. It is features a melting point of 217 °C. The reservoir was heated up to 330 °C to melt the solder inside. Nitrogen was used as both actuation gas and rinse gas to actuate the jetting and shield the jetted molten solder flow, respectively. Polyethylene terephthalate (PET) foil with a layer thickness of 125 µm was used as the demonstrating substrate. The PET foil was heated up to 80 °C by a hot plate during the printing. During the printing, the printhead had a traversing speed of 300, 600, or 900 mm/s and 1 mm printing distance.

Characterization methods

The scanning electron microscope images were taken by Phenom Pro SEM machine at 10 kV acceleration voltage. Before the measurement, the whole samples were coated with a few nanometer gold via sputtering to increase the electrical conductivity, resulting in higher imaging resolution.

The line resistance was determined by a four-point measurement (Karl Suss PM5). Current was applied in the range of 5 to 100 mA while voltage was measured. The overall resistance of printed lines was then calculated based on Ohm´s law.

The shear tests were performed by a Nordson Dage 4000 Bondtester machine. A Ball shear routine with a BS5kg tool cartridge was utilized. For all tests, the shear forces were recorded by applying a constant shear rate of 0.5 mm/s until the printed lines were sheared off from the polymer substrates.

Results and discussion

To test the printing parameters, different traversing speeds were tested to evaluate the line printing performance regarding line shape and adhesion. Traversing speeds of 300, 600, and 900 mm/s were selected. The corresponding microscope images of printed lines on PET foil are shown in **Figure 2**. The traversing speed highly influences the line formation, which shows very similar behaviors as inkjet-printed lines from individual droplets [16,17]. The StarJet was operating at Jet mode [11], where a constant molten solder flow is ejected from the nozzle orifice at a fixed flow rate. For low traversing speeds of the printhead, for example at 300 mm/s, a very strong bulging is formed (see **Figure 2**a). When the printing speed increases, for example to 600 mm/s, the bulging effect is reduced, as shown in **Figure 2**b. When an appropriate printing speed has been reached, which is 900 mm/s in this case, a straight and uniform line can be deposited on the PET foil (see **Figure 2**c). After a proper printing speed has been found, uniform lines can be printed with different linewidth via different nozzle orifice diameters, as shown in **Figure 2**c&d. They were printed from nozzle chips with an orifice diameter of 180 and 60 µm, respectively.

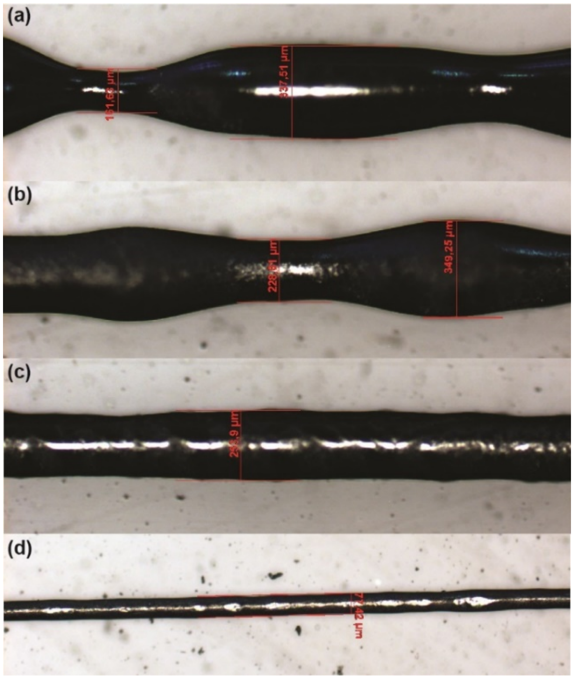

***Figure 2** Microscopic images of printed solder lines on PET foils via StarJet technology. They were printed from two different nozzle chips with orifice diameters of (a-c) 180 µm and (b) 60 µm, and different traversing speed of (a) 300 mm/s, (b) 600 mm/s, and (c & d) 900 mm/s.*

Flexibility is one of the key advantages of polymer electronics. As illustrated in **Figure 3**, the printed solder lines shows excellent flexibility and high stability on the polymer substrate. Although the solder was heated up to 330 °C in the reservoir with a printing distance of 1 mm, the polymer substrate did not show any visual damage by the printing process. The polymer foil was bent at radius of around 5 mm for more than 10 times, and no line breaking and de-attaching of the printed line on substrates have been observed.

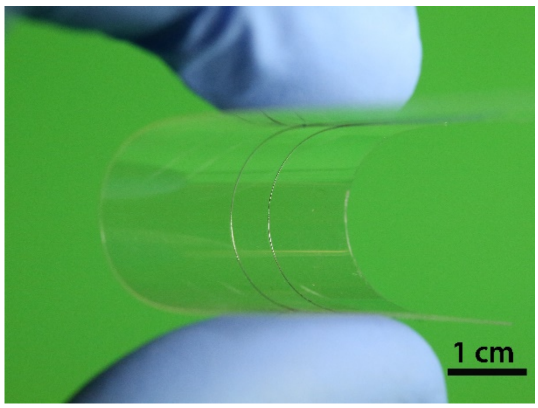

***Figure 3** Photograph of a bent PET foil with two printed solder lines at a green background. The solder lines were printed via StarJet technology at traversing speed of 900 mm/s.*

The adhesion property of printed solder lines on the PET foil was characterized quantitatively by a shear-off measurement. It showed that a maximum force of around 3.5 N is required to shear the printed lines off the PET substrate. The adhesion property is far better than the inkjet-printed silver structures on polymer substrates, where it was reported that the thin films can only withstand an adhesive tape test after strong sintering process [18]. Even a screen-printed silver paste, after thermal sintering at 300 °C for 30 min, can only withstand a critical force of around 1.4 N [19].

Electrical conductivity of the printed solder lines was characterized by a 4-point-probe setup. The measurement result of the printed line with a linewidth of ~250 µm is depicted in **Figure 4**. A resistance of 37.4±0.08 mΩ was measured over 5 mm line length. It can be seen that there is a nearly perfect line fitting between provided electric current and measured voltage. In other words, it exhibits an ohmic resistance.

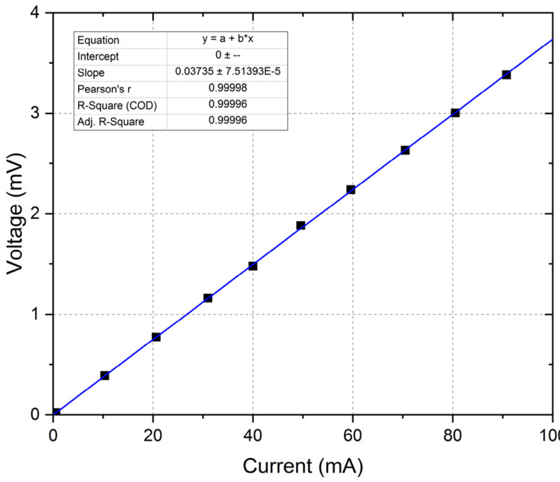

***Figure 4** Voltage – current measurement diagram of one printed solder line at traversing speed of 900 mm/s with a nozzle orifice diameter of 180 µm. It was measured by a 4-point-probe setup. The blue line indicates the linear fitting of the measured data. The fitting analysis is attached in the inset table.*

To further understand the strong adhesion of printed solder on PET foils, printed solder lines were completely or partly peeled off from the PET foil and imaged by SEM. As it can be seen from **Figure 5**a, a small imprint on the PET foil was created by printing the molten solders. A closer observation on the PET foil where the printed solder line was located before being peeled off is depicted in **Figure 5**b. It can be clearly seen that the printed solders slightly burned into the PET foil and lead to a partly melting of the polymer and re-structuring. The bottom side of the peeled-off solder line was also imaged by SEM (see **Figure 5**c&d). The bottom side of the printed solder line has relative flat surface instead of natural half cylinder shape. This indicates the molten solder had strong interaction with the flat PET thin film. With much higher magnification, there are evenly distributed small grains (less than 5 µm diameter) all over the back surface of the printed solder line. It matches very well with the reformed network microstructures on the PET surface from where the printed solder line was peeled off (see **Figure 5**b). It can most likely be concluded that these reformed 3D inter-connected microstructures between printed solder and polymer substrates lead to high adhesion and therefore high mechanical stability of printed solder on PET foils. Due to the high flexibility of the PET foil and solder, the printed solder lines also exhibit high flexibility and bendability on PET foils, as depicted in **Figure 3**.

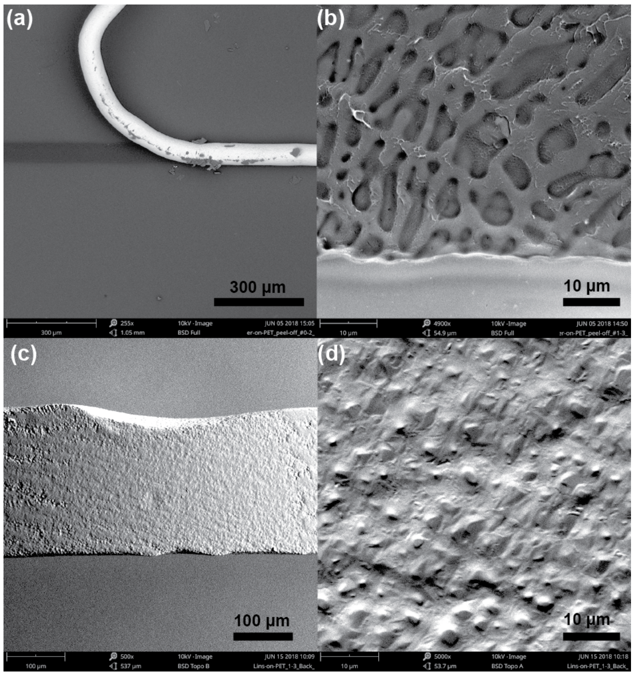

***Figure 5** Scanning electron microscope (SEM) images of a printed solder line on a PET foil via StarJet Technology: (a) A printed solder line is half-peeled off from a PET foil. (b) A close imaging on the PET foil where printed solder lines was peeled off from graph (a). (c) The SEM image of the bottom side of a printed solder line, which was peeled off from the PET foil. (d) a higher magnification imaging of the bottom side of the printed solder line from graph (c).*

Summary and conclusion

We have demonstrated that flexible solder lines can be direct printed onto polymer substrates (PET foils) via StarJet Technology. The solder lines were direct printed from pure solder material under ambient conditions, which provides a highly cost-efficiency metal line deposition on flexible substrates. With interchangeable nozzle chips, featuring different orifice diameters, different line-widths can be achieved via StarJet technology. In this work, solder lines with linewidths of ~70 and 250 µm were printed on PET foils. A high traversing speed of about 900 mm/s is required to realize straight thin lines. Printed lines exhibit high mechanical stability, enduring shear forces up to 3.5 N. Moreover, low electrical resistance of about 37 mΩ for a 5 mm long line was demonstrated. A high bending radius of ~5 mm can be achieved and the bending induces no negative influence on electrical conductivity. The strong adhesion was examined by the SEM measurement. It reveals that the printed solder lines form 3D micro grains on the solder surface, and the PET polymer surface was also partly melt and reformed a matching microstructure network during the printing process. The high adhesion originates most likely from these close microstructure inter-connections between the solder line surfaces and PET polymer surface.

The high flexibility and stability of printed solder lines on polymer substrates enables high application potential in flexible and wearable electronics. The low material cost and one-step process provide additional economic advantages. For example, it could be used for providing electrical power to printed functional units on polymer substrates. It can also be used to interconnect organic and printed electronics components in traditional silicon-based microelectronics for complex functionalities on flexible substrates.

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Author Biography

Zhe Shu obtained his master of science in photonics at the Friedrich-Schiller-University Jena in Germany in 2011. From 2012, he worked as a scientific researcher in Fraunhofer institute for applied optics and precision engineering (IOF), where he focused on direct integrating multi-functionalities such as fluorescence light sources onto microfluidic chips as well as developing fast prototyping of 3D optical elements via inkjet printing technique. He obtained his PhD degree in the meantime. Since 2018, he is working as a postdoc in Laboratory for MEMS Applications, IMTEK, University of Freiburg on the topic of further developing the StarJet printing technology.

Björn Gerdes obtained a master of science in microsystems engineering from Albert-Ludwigs-University Freiburg in Germany in 2013. Since 2013, he is a research scientist at the Laboratory for MEMS Applications, IMTEK, University of Freiburg where he focuses on direct metal printing via StarJet technology. In this field, he developed drop-wise printing of aluminum alloys and different applications of the StarJet technology.