A Hybrid Approach Combining 3D and Conductive Inkjet Printing for the Generation of Linear Ion Traps for Mass Spectrometry Applications

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Abstract

Printed conductors have attracted strong interest in academia as well as the industry. While first applications using printed conductors on flat as well as curved surfaces are establishing in the market, extensive research still is conducted on the post-processing technologies needed for high-volume fabrication of solution processed conductors.

With regards to the potential low-cost, high-throughput manufacturing of conductors on inexpensive polymeric foils, new applications start to evolve that call for an even more elaborate investigation of the printing and post-processing steps included. This paper assesses the potential of inkjet-printed conductors for the use in low-pressure environments, such as linear ion-traps for mass spectrometry. In these environments remainders of trapped air or organic solvents affect the performance and lifetime of the getter pump systems used. Additionally, high frequency characteristics of the processed conductors are investigated as these are essential for the sensitivity of an ion trap.

In this contribution we establish the framework for the application of conductive inkjet printing on curved surfaces for sensing application in low-pressure environments. Inkjet-deposited nanoparticle inks were investigated with respect to their characteristics under vacuum conditions. The deposits on polymeric foils as well as on DLP processed three-dimensional semi-finished parts were subjected to thermal post-processing and measured with respect to their electrical characteristics as well as their outgassing behavior.

Introduction

Portable mass spectrometers are of high interest for a number of applications including automotive, medical, food and security. With the limitation to application-targeted molecules there is no necessity for acquiring a full spectrum and, hence, the instrument can be operated in a non-scanning mode [1]. This selective ion monitoring offers the potential of higher sensitivity, simpler control electronics, smaller size, lower power consumption as well as lower cost.

Another approach to reducing the weight as well as the cost of such an instrument for in-field application is to explore alternative production techniques and materials for the mass analyzer. Linear ion traps (LIT) with hyperbolic electrodes provide a highly sensitive measurement technique for a wide range of substances. The complex hyperbolic shape of the electrodes as well as the resulting weight of the final component, which are typically manufactured by CNC-machining of conventional steel, offers a great opportunity for alternative manufacturing techniques such as 3D printing. While polymer-based 3D printing such as Dynamic Light Processing (DLP) is a versatile production technique for reasonably complex shapes it is not capable of inline creation of conductive features or the surface finish usually required in LIT manufacturing.

In this contribution we present a hybrid approach to the generation of LIT electrodes by combining DLP and inkjet printing of metal nanoparticle inks.

Experimental

3D printing was performed with an Envisiontec Perfactory 3 Mini Multi Lens with Enhance Resolution Mode (ERM), using 700 mW/dm^2 of visible light at 15 µm – 100 µm thick layers. The smallest ERM voxel size was 16 µm. Dynamical mechanical analysis was performed using a TTDMA (Triton Technology Ltd, UK).

Inkjet printing was performed using a Xaar126-50 pL printhead jetting EMD 5603 (SunTronic, SunJet, UK) with an optimized waveform. Sintering was performed in a convection oven (Binder, US). Two-point resistance measurements were conducted using a lab multimeter (UT33D, UNI-T, CN). High frequency impedance was evaluated using a precision impedance analyzer Agilent 4294A in a frequency range between 40 Hz and 1 MHz. Measurements were conducted using manual probes (Cascade DPP105-M-AI-S) equipped with 7 µm tungsten tips.

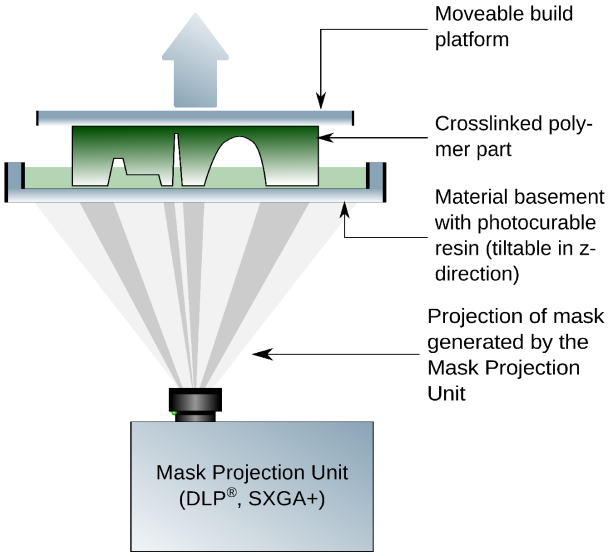

Figure 1: Schematic overview of the 3D printing process.

DLP Processing of LIT Electrodes

DLP is a rapid manufacturing technique for selective curing of photosensitive resin using a dynamic masking capability. The process uses specific rip software in order to translate a CAD model (cf. Figure 2) into slices of specific thickness. Using a DLP-based projector (cf. Figure 1) the photosensitive material is locally cured on a build substrate, which then is moved up by a defined distance in order to process the subsequent slice. This process is repeated until the part is completed.

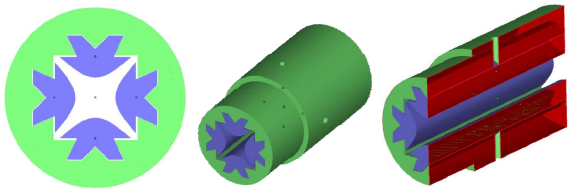

Figure 2: CAD fabrication drawings for DLP LIT assembly a) 2D top view (green – LIT housing, blue – LIT electrodes), b) 3D view, c) 3D cross section.

Photosensitive Materials

The materials used for the generation of the bodies as well as the linear ion trap electrode base where provided by EnvisionTEC (Gladbeck, DE). In order to study the suitability for the anticipated application, test structures were fabricated and subjected to dynamical mechanical analysis at a nominal frequency of 1 Hz and a temperature range of 22 °C to 200 °C. The results are depicted in Figure 3 for three different materials – *R11*, *HTM140-V1* and *HTM140-V2*, respectively.

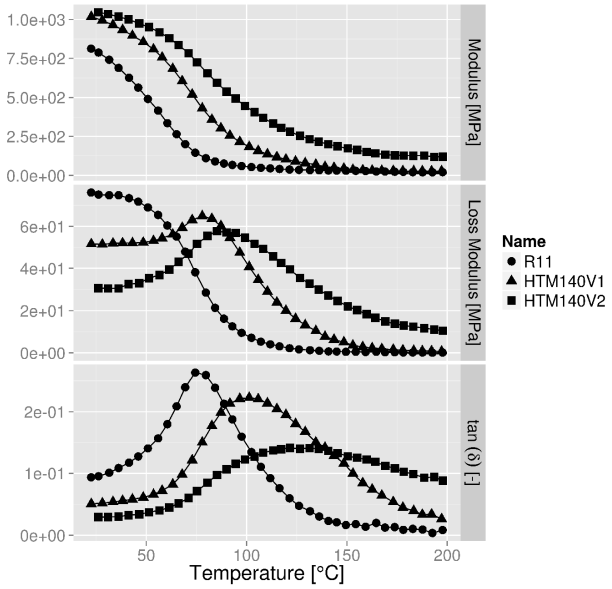

Figure 3: Results of Dynamical Mechanical Analysis of 3D-printed materials as a function of temperature (● – R11, ▲– HTM140V1, ■ – HTM140V2).

The results clearly indicate varying moduli for the different materials as a function of the temperature. The transition temperatures, indicated by the peak in the loss tangent *tan(δ)*, were measured lowest for the material *R11* and shifted towards higher temperatures with *HTM140V1* and *HTM140V2*. This indicates a better thermal stability for *HTM140V2* and also enables the sintering of inkjet printed nanoparticle inks in the range of 100 °C to 150 °C on the surface of these produced parts without damage of the substrate.

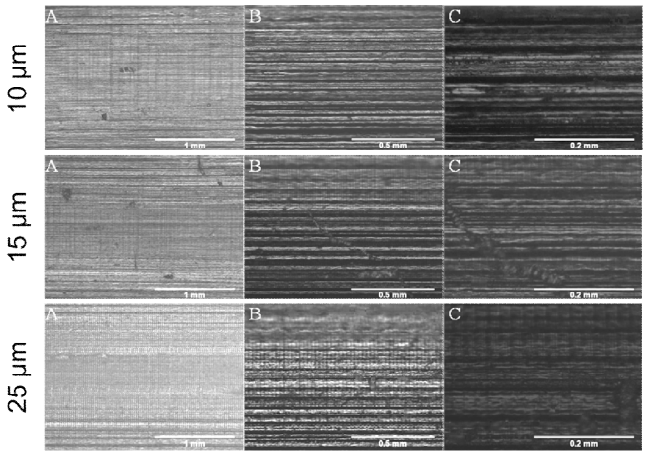

Figure 4: Surface finish of 3D-printed LIT electrodes with different stepping distances in z-direction (left to right) at various maginifactions (scale bars: A - 1 mm, B - 0.5 mm, C - 0.2 mm).

Figure 4 shows the resulting surface quality when using different step sizes of the build platform in the process described above. The results are depicted for a z-step of 10 µm, 15 µm and 25 µm, respectively. The analysis clearly showed a predominant texture in direction of the building process (left to right in the images). This texture was independent of the z-stepping of the build substrate during generation of the investigated parts and showed height variations of up to 25 µm. The influence of the stepping distance could, however, be observed perpendicular to build direction. Up to a stepping distance of 15 µm no clear influence of the stepping distance could be observed and could therefore be neglected. At 25 µm, however, a two-dimensional texture appeared which clearly had the periodicity of the movement of the build-substrate. The planarization of the electrode surface is of high importance as variations in the field distribution inside the ion trap may promote undesirable ion heating. For this reason, a planarization step may be necessary for the application of these electrodes in a mass analyser.

After DLP fabrication, the ceramic resin rods were coated with metal to provide conductivity and further improve the surface finish of the electrodes. Smooth electrode surfaces are essential for providing consistent RF field for mass analysis. Two different approaches were chosen for generation of the conductive top coating. A 1 µm thick gold sputtering was compared to an electroplating method (Metalise™, 3DDC Ltd, UK) which in a first step deployed a 130 µm thick copper/nickel film and subsequently applied a surface finish using a 300 nm thick layer of gold. It was found that sputter coated rods had acceptable surface finish with a rather high resistance of 160 Ω. The electroplated electrodes had significantly better surface finish and a total resistance of well below 1 Ω.

Inkjet Surface Coating of LIT Electrodes

For the inkjet printing of the LIT electrodes the printhead was positioned to yield 360 dpi x 360 dpi resolution [2], and operated at 1 kHz firing frequency resulting in a feed rate of 50 mm s^{-1}. To produce electrodes of different thicknesses and lower resistances, one through five layers were printed. For such multi-pass mode, the prints were aligned in an interleaving fashion thus increasing

the print resolution and providing a laterally more homogeneous electrode layer thickness. The printing was performed wet-in-wet, i.e. without intermediate drying. The LIT electrode bodies were kept at room temperature during printing.

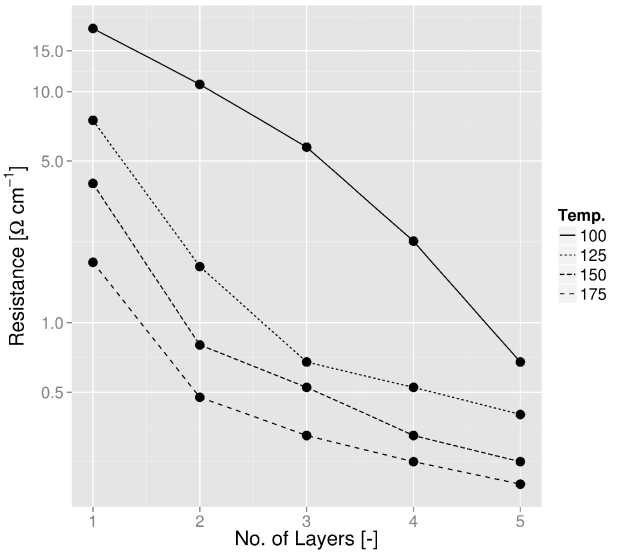

Figure 5: Development of resistance as a function of number of printed layers and sintering temperature [holding time: 30 minutes, substrate: polyimide].

Electrical Performance of Sintered Structures

In view of the thermally sensitive polymeric LIT electrode bodies it was investigated whether low oven sintering temperatures could be applied. Temperatures used were 100 °C, 125 °C, 150 °C and 175 °C, and the duration of the sintering process was kept constant at 30 min. Temperatures of 200 °C and beyond led to mechanical deformation and delamination between layers of the cured material during the extended heat exposure and were therefore not further considered. The resistance *R* of the printed and sintered electrodes was measured using a 2-point measurement over the whole length of the LIT electrodes. The results normalized to one centimeter are summarized in Figure 5. It was observed that oven heating for 30 min at 100 °C left a partially wet surface, hinting at insufficient sintering conditions, which can be clearly seen by the deviant development of the resistance as a function of the layer thickness. It was further observed that printing single pass at 360 dpi x 360 dpi resulted in insufficient coverage in some areas of the LIT electrode. Such holes in the otherwise full coverage were most likely caused by local de-wetting, which occurs when the surface tension of the fluid is considerably higher than the surface energy of the substrate. De-wetting in single pass printing could be avoided by pre-treatment of the substrate with plasma, corona or UV-irradiation, which would increase the surface energy of the substrate. In the present investigation the de-wetting was avoided by multi-pass printing in interleaving mode so that the open areas, typically occurring between tracks, could be covered in the consecutive print pass. For the initial production of sample LIT electrodes a combination of three layers and a sintering temperature of 150 °C were chosen as a suitable trade-off, resulting in a total LIT electrode resistance of ~2 Ω, which is relatively close to the plating results discussed above at only a fraction of the layer thickness.

Alternative samples were fabricated using the same settings as described above but on a flat 25 µm polyimide substrate in order to investigate the high frequency characteristics between 40 Hz and 1 MHz. Simple microstrip structures with accompanying probe pads were used for this investigation, where the size of the contact pads was chosen in such a fashion that its resistance was negligible to the resistance posed by the four pixel wide lines connecting them. The measurement revealed that the DC resistance changed with the increase in cross-sectional area in an expected fashion. The high-frequency component revealed inductive behavior, increasing the magnitude of the impedance noticeably from 50 kHz onwards. In order to further assess the recorded behavior, the general model of an RL-circuit

$$|Z|=(R^2+(\omega L)^2)^{1/2} \quad (1)$$

was fitted to the data and the equivalent circuit parameters *R* and *L* were extracted. The results are depicted in Figure 6.

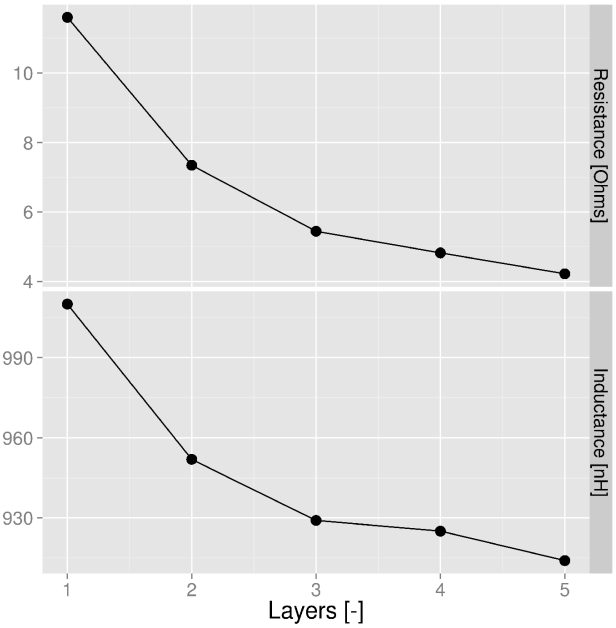

Figure 6: Equivalent resistance and inductance of four pixel wide lines on 25 µm thick polyimide substrates [Sintering temperature: 150 °C].

The equivalent series resistance *R* decayed as expected with a reciprocal behavior. This is in line with the increase in area and the resulting resistance. The change in the inductance showed a much lower reciprocal behavior, which corresponds to the behavior of a microstrip. The inductance can be estimated using

$$L=\mu dl/w \quad (2)$$

where μ is the magnetic permeability, d is the thickness of the track, l is the length of the track and w represents the width, respectively [3]. As μ and l could be assumed constant during the conducted experiments, only d and w were left as variables. From the behavior of the equivalent inductance one could therefore conclude that the increase in width is much stronger than that in height, wherefore the inductance decreases. This behavior is particularly strong in the transition from one through three layers, and seems to stagnate between three and four layers, where the height increased roughly as much as the width. Thereafter, an

additional layer seemed to introduce further spreading rather than an increasing height. As an assessment of the samples revealed no noticable increase in width, the mayor change resulting in the stronger decrease of the inductance must originate from a reduction in thickness and could relate to the relatively strong coffee ring effect observed with the used ink.

Outgassing Tests

In order to establish an understanding of the compatibility of the printed and sintered metal structures for the applications in a low pressure environment, outgassing tests were performed by measuring and analyzing the substances emerging from a heated sample in a vacuum chamber. Therefore samples of polyimide (2x2 cm^2) were coated with 3 layers of silver nanoparticle ink (1x1 cm^2) and sintered at temperatures of 100 °C and 200 °C. Polyimide specimens of comparable size were measured as baseline. Figure 7 presents the results for various molecules emerging for the samples at different temperatures.

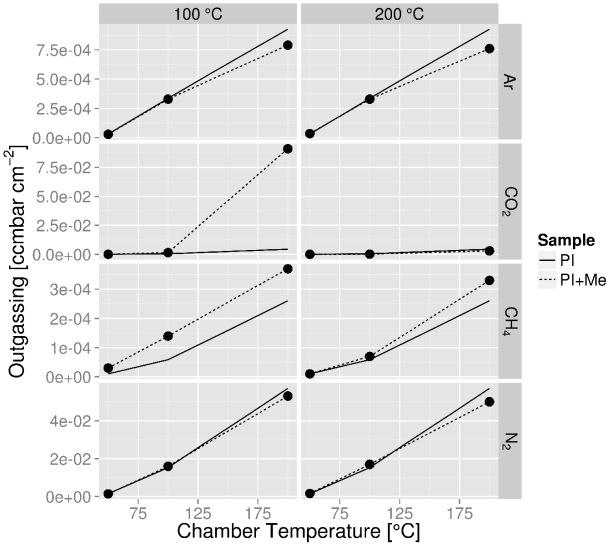

Figure 7: Outgassing as function of chamber temperature for polyimide material with (PI+Me) and without (PI) metal coating for different curing temperatures of the metal nanoparticle ink.

All the tested samples released nitrogen as the main gas. As the outgassed quantities were comparable among the samples, it is believed that nitrogen is released by the polyimide substrate. Slight reductions in the values for the metal-coated samples may suggest a sealing of the polyimide surface and an inhibition of outgassing from these surfaces. Furthermore, the ratios of nitrogen to argon suggested that the samples released trapped air. The only noticeable difference was found with the sample being cured at 100 °C which released a large amount of CO_2. This may indicate the insufficient thermal energy for sintering discussed above and therefore may relate to remainders of organic solvents.

Comparative studies using the 3D printed material HTM140V2 showed only a small rise in the base pressure of the system of 2 x 10^{-6} Torr. Nitrogen and CO_2 were found to be most abundant, while argon and methane were present in low amounts.

Conclusion and Outlook

The presented work provides a first insight into the hybrid application of 3D printing and conductive inkjet printing for the manufacturing of low-cost, low-weight linear ion traps for the application in portable mass spectrometry devices.

Digital Light Processing was used in conjunction with a ceramic photocurable resist (HTM140V2) to produce hyperbolical LIT electrodes, which showed sufficient thermal stability and accuracy for the anticipated application. Surface finish was found to be the major challenge and was improved by changing the step size of the build platform. A special electroplating technique was employed to generate a full conductive coating of the electrodes as a benchmark for the inkjet printed top coating. Using a 130 µm thick nickel/copper coating and a 300 nm gold finish the measured resistance was well below 1 Ω over the ~40 mm long electrodes.

Inkjet printing was found to provide low resistances with increased numbers of layers as well as interleaved printing at 360 dpi x 360 dpi resolution. The chosen process parameters of three printed layers and oven sintering at 150 °C for 30 minutes enabled the production of LIT electrodes with a total resistance of 2 Ω along the whole electrode. Outgassing experiments on the printed samples showed that with sufficient sintering negligible amounts of gas are released, which indicated the applicability of the printed structure in low pressure environments.

Further investigations will consider system integration and improvement of the performance of LIT electrodes by optimizing the surface structure of the 3D printed components as well as using phonic sintering to overcome the temperature restrictions of the materials used.

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References

[1] B. Brkić, S. Giannoukos, N. France, A. Janulyte, Y. Zerega, S. Taylor, "Modeling of an ion source lens system for sensitivity enhancement in a non-scanning linear ion trap", International Journal of Mass Spectrometry 353 (2013) 36.

[2] W. Voit, W. Zapka, and A. Menzel, "Inkjet printing of phase-change materials," NIP Digit. Fabr. Conf., 2008.

[3] M. Thompson, "Inductance Calculation Techniques - Approximations and Handbook Methods," Power Control Intell. Motion, 1991.

Author Biography

Ingo Reinhold graduated in micromechanics-mechatronics with emphasis on print- and media technology from Chemnitz University of Technology in 2008. After joining Xaar's Advanced Application Technology group in Järfälla, Sweden, he focused on advanced acoustic driving of piezo-type inkjet printheads alongside with pre- and post-processing of functional materials in digital fabrication. He is currently enrolled as a PhD student within the iPack VINN Excellence Center at the Royal Institute of Technology (KTH) in Stockholm, Sweden.