Inkjet Printing of Bioresorbable Materials for Manufacturing Transient Microelectronic Devices

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Herein, the inkjet printing of bioresorbable materials tuned to function as electrode, dielectric, and semiconductor layers is reported, thereby developing multilayered microelectronic devices such as capacitors and thin-film transistors, potentially applicable to address specific medical needs. Polymers and natural materials, e.g., poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), shellac, and β-carotene, indigo inks are implemented using jettable formulations, that are either commercially procured or self-formulated, designed explicitly to deposit fundamental layers for capacitors and transistors. Several parameters are evaluated and adjusted to precisely define a layer’s thickness, topology, and geometry, matching with the properties of a fully biodegradable Ormocere substrate, explicitly developed for the specific biological applications. Furthermore, these parameters support in acquiring the intended electrical properties of layers, i.e., conductivity, insulation, semiconductivity, capacitance, and current versus voltage characteristics. The entire manufacturing process of devices is accomplished on the Ormocere substrate under ambient conditions and below 60 °C. The results exhibit that the electrical characteristics of the printed functional layers and devices show direct influence to the physical geometry of the printed features. A fully printed capacitor demonstrates capacitance of 1 nF cm⁻², whereas transistors show p-type and n-type characteristics with current 0.18–5 μA and mobility 6 × 10⁻⁴–7 × 10⁻² cm² V⁻¹ s⁻¹.

1. Introduction

During the past decade, printed electronics has seen its application entering into different sectors, e.g., wearable and stretchable electronics, flexible, and hybrid electronics such as organic photovoltaics, batteries, multilevel sensor and detector applications and conductive interconnects in the industries related to system packaging.[11–17] Due to the numerous benefits such as deposition accuracy in micrometer scale, industry relevant up-scalability, and efficient technique of digital processing, the inkjet printing technology is widely recognized as a smart digital fabrication tool for developing microelectronics on various polymeric substrates.[8–11] Several kinds of flexible electronics have already been manufactured using the inkjet printing technology, e.g., capacitors, thin-film transistors (TFTs), resistors, sensors and detectors, radio frequency antennas, photovoltaics, and so on.[4,5,7,9–16] All these printed applications are clear evidences to validate the implementation of inkjet technology to deposit fundamental layers with electronic properties, i.e., conductors using nanoparticle or particle-free-based metallic or polymeric inks, dielectrics by polymer-based or hybrid inks with embedded nanoparticles and organic semiconductors (SCs).[11,12,17,18] Although, the printing of these novel materials has always been a big challenge, but due to the continuously evolving market scenario, it has recently become possible to deposit and postprocess (curing/sintering) these materials with high reliability, thereby, satisfying the electrical demands of devices and circuits, e.g., passive device circuit, filter circuit, and photodetectors.[14,19,20] This has resulted in the quest for the inkjet technology to get engaged into several other sophisticated and challenging fields like medical implantation and prosthetics.[21–24] The field of medical implantation is vast, out of which some of them do not really require printed devices to remain in the body for an extended time duration. On the contrary, some of these medical implants require only diagnostic monitoring for a defined time interval, and/or some of them only reciprocate electrical signals to stimulate certain human body functions, e.g., motoric and neurological communications, only for few times just after a performed medical surgery. It becomes at times very inconvenient for certain medical cases (after sophisticated medical operations), wherein the patient is reoperated for verifying either the status of the recovery or process triggering for the stimulation. The inkjet printing process typically proceeds...
under a controlled environment (enclosed ink delivery) without any traces of contamination, and hence it qualifies optimally for the deposition of biodegradable ink materials (e.g., biocompatible and biodegradable).

During the past few years, many research groups have attempted to explore natural materials (with or without solution-processable capability) that also possess electronic properties. Some of the explored materials by Irimia-Vladu et al.\textsuperscript{[25,26]} listed in the literature are shown in Table R1, Supporting Information. Some of discussed substrates are paper, silk, protein-based gelatin, polysaccharides poly lactic acid (PLA), starch Ecoflex BASF, etc., whereas poly(thiophenes), polyaniline, poly(pyrrole), and poly(3,4-ethylenedioxy thio phene) polystyrene sulfonate (PEDOT:PSS) were used as conductors; shellac, caffeine, polyvinyl alcohol (PVA), various sugars (sucrose, lactose, and glucose), nucleobases, i.e., adenine and guanine as dielectrics; and indanthrene–yellow G (I–y–G). Indanthrene–brilliant Orange RF (I–b–O RF), zinc oxide (ZnO), C\textsubscript{60}, indigo, pentacene, \(\beta\)-carotene, and perylene diimide as SCs. In contrast, the research in solvent-based biodegradable inkjet ink formulations is insufficient. However, the research papers reporting on the inks related to various other deposition techniques, e.g., gravure, offset, flexography, microcontact, dry transfer printing technologies, and so on can be used for generating formulations of biodegradable inkjet inks.\textsuperscript{[27]} As follow up, through this publication, we want to demonstrate the development of the inkjet printable inks, which are biodegradable and electronically functional for manufacturing active and passive devices. To accomplish this aim, we have screened various published works that contribute as basis for our present investigation. A list of research works dedicated to the manufacturing of devices, materials used, processing conditions, and device performance are shown in Table R2, Supporting Information.\textsuperscript{[26–40]}

Recent advancements reported during the past 3 years toward transient electronics have been immense. Feig et al.\textsuperscript{[41]} and Li et al.\textsuperscript{[42]} showed series of different functional materials (organic and inorganic) that are being used conventionally for manufacturing biodegradable electronics. Verma et al. demonstrated the development of a biodegradable silylated agarose substrate that is compatible for photolithography and manufacturing flexible and printed electronics.\textsuperscript{[43]} Feng et al. showed the utilization of an optimal laser-sintering tool for processing screen-printed conductive Zinc (Zn) layers, demonstrating a suitable conductivity for developing electronics.\textsuperscript{[44]} Zhang et al. showed the implementation of biodegradable conductive Fe microparticles in a polycaprolactone (PCL) insulating matrix polymer composite for the application in interconnects within various sensing devices.\textsuperscript{[45]} Lee et al. showed paper-based organic thin film transistors, that are explicitly claimed as biocompatible, biodegradable, and most environment friendly.\textsuperscript{[46]} Xiang et al., in contrast, described the degradable electronics including devices with high yield and uniformity for environmental monitoring purposes, e.g., temperature and moisture.\textsuperscript{[47]} Gao et al. described the development of transient electronics for which the degradation is triggered by moisture.\textsuperscript{[48]} Here, active and passive devices were manufactured, e.g., TFTs, diodes, resistors, capacitors, antennas, resistive memory, and polyanhydride substrate. The device fabrication involved the deposition of materials by Kapton film-based shadow masks along with other conventional processes and materials, e.g., Al, copper, nickel, magnesium oxide (MgO), and indium gallium zinc oxide (IGZO). The degradation of devices happened in 40 h or more by phenomenon hydrolysis along with the generation of organic acids in contact with moisture and in situ digestive processes.\textsuperscript{[49]} Kang et al. presented a review article that describes about biodegradable (moisture, ultraviolet [UV], heat, and other parameters) flexible and stretchable organic and inorganic electronic devices. Several devices on degradation basis are discussed from active, passive, reactive, sensor, to energy generation, and storage components. The deposition was carried out using lithography, plasma-enhanced chemical vapor deposition (PECVD), atomic layer deposition, electron-beam and thermal evaporation, etching processes, etc. Materials such as MgO, single-crystal SiO\(_2\), silicon, Mg, molybdnum (Mo), silk, cellulose, cyclic poly(phthalaldehyde), cyclododecane, poly(lactic-co-glycolic acid) (PLGA), PVA, SiN\(_x\), Al\(_2\)O\(_3\), sugars, nucleobases (adenine and guanine), caffeine, 5,5-’bis-(7-dodecyl-9H-f luoren-2-yl)-2,2’-bithiophene (DDFFTF), IGZO, eumelanin, \(\beta\)-carotene, I–y–G, and I–b–O RF, perylene diimide were utilized.\textsuperscript{[47]} Apart from this, certain advancements have also been special. Li et al. exhibit the development of novel biodegradable alloy material based on Zn metal.\textsuperscript{[48]} Tong et al. show the development of biodegradable Ag nanowire-based cellulose film adapted for the flexible electroluminescent devices.\textsuperscript{[49]} Khalid et al. demonstrated biodegradable piezocapacitive pressure sensor using composite of PLGA and PCL, Fe–Zn bilayer electrodes, PVA substrate for low-pressure measurement in tactile range of 0–5 kPa. For such sensors, degradation was noted in less than 1 week.\textsuperscript{[50]} Curry et al. exhibited the development of biodegradable piezoelectric force sensor using Mo, PLA, and piezoelectric poly-v-lactide.\textsuperscript{[51]} Next to this, She et al. described the biodegradable battery featuring a solid electrolyte of sodium chloride and PCL, along with other materials, e.g., Fe/Mg complex and PLA.\textsuperscript{[52]} Lee et al. showed the facile fabrication of super capacitors that is fully biodegradable and stretchable using electronic materials such as Mo, PVA-based gel polymer electrolyte, and biodegradable elastomers. A review article from La Mattina et al.\textsuperscript{[53]} reported numerous biodegradable materials and devices. Out of which, inorganic and organic TFTs are developed, using substrates such as silk, silk fibroin, silicon nanomembrane, PLGA, polysaccharide, silicon on insulator wafer, caramelized glucose, gelatin, shellac; dielectrics, e.g., SiO\(_2\), MgO, PVA, silk fibroin, glucose, caffeine, or adenine–guanine; SCs such as c-Si, ZnO, DDFFTF, perylene diimide, 3,3’-dihexyl-2,2’-5’2’,5”-2’-quaterthiophene, gallium indium zinc oxide, I–y–G, I–b–O RF, \(\beta\)-carotene, indigo, synthetic-conjugated polymer decomposable polymer from diketopyrrolopyrrole; and electrodes, e.g., Au, Mg, tungsten, Ag, indium tin oxide, Al, Fe, and Zn. The layers were deposited with photolithography, reactive ion etching, PECVD, thermal evaporation, spin coating, and anodization techniques. The device performance varied with \(V_{th} = 0.2–20\) V, \(\mu_{fe} = 0.013–630\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) depending on p- and n-type SCs and device architecture.\textsuperscript{[54]}

When all the works from the several researchers are compared among each other, it can be said that the missing research area is the exploitation of a solution-processable technique that enables the user to digitally control the deposition of thin films that facilitate manufacturing devices with more practicality and modularity to medical implants. Some of the major benefits are the
utilization of different sizes and shapes, short manufacturing numbers, device architectures, different material choices, tuning of deposition and postprocess parameters with minimum wastage, integration to a suitable diagnostic peripheral for data extraction for further analysis, and most importantly that all the devices are bioresorbable under specific biological environment. Herein, we attempt to demonstrate the utilization of the inkjet technology for printing some fundamental electronic layers and thereby develop conductive tracks, capacitors, and TFTs. The investigation presents here an extension of the preresearch done by Mitra et al., conducted in the same field but shows only a proof-of-concept printed layers with the process validation of the inkjet inks aiming at the development of conductors, dielectrics, and SCs. In this article, the focus has been put forward to investigate the use of PEDOT:PSS as conductor, shellac as dielectric along with β-carotene and indigo SC inkjet ink formulations, for the development of capacitors and TFTs on the innovative biodegradable Ormocere substrate. Furthermore, the goal is to achieve respectable performance from the printed devices compared with the ones, which are existing in the literature (operating <40 V). This was done by evaluating different relevant printing and curing parameters suiting to the fragile biodegradable substrate, overcoming the morphological or topological challenges for the printed layers and investigating the scope of these optimizations for specific electrical demands.

2. Experimental Section

The well-known material inkjet printer DMP-2831 from Fujifilm Dimatix along with 10 pL-based dimatix materials cartridges were utilized for developing the printed functional electrodes, dielectrics, and SC layers, and furthermore, capacitor and TFT devices. The necessary print patterns were designed digitally using defined dimensions to obtain maximum accuracy and precision during the printing process that would result into desired electronic properties. Figure 1A,B shows a typical inkjet deposition process for manufacturing capacitors and TFTs.

For developing capacitors, the dimensions related to the pattern layouts for the bottom and top electrodes were kept constant and simplified to $5 \times 5 \text{ mm}^2$, whereas the dimension of the dielectric layer was slightly extended. In contrast to this, the digital patterns related to the TFTs constituted $0.5 \times 0.5 \text{ mm}^2$ for the three contact pads, 0.15 mm-wide interconnections, 1 pixel line-based interdigitated source/drain (S/D) electrodes separated with 50 μm (channel length $L$) and S/D length of 1 mm (channel width). Hence, the calculated $W/L$ ratio is 20. For the development of both the devices, conductive electrodes were deposited with PEDOT:PSS using a water-based Clevious F-HC Solar ink (1–1.5 wt%) from Heraeus. Unlike, the commercial PEDOT:PSS ink, the dielectric ink based on shellac due to unavailability could not be acquired directly. To obtain an inkjet printable dielectric ink formulation that could be utilized for developing microelectronic devices, the focus was explicitly set to involve different solvents and solid contents. Polymer-based wax-free shellac granulate was purchased from Sigma Aldrich. During the process of ink formulation, care was taken that the shellac granulate is dissolved appropriately in the solvents ethylene glycol or water–ethanol mixture (1:1) or propylene glycol methyl ether acetate (PGMEA), with shellac loading ranging between 1 and 10 wt%, along with continuous stirring using magnetic bars for 3 h at 100 °C. Further details about the tested ink formulations A–J are shown in Table 1.
As mentioned earlier, off-the-shelf bioresorbable organic SC inks for inkjet technology so far has not existed, therefore, two SC inks were formulated based on β-carotene and indigo (powder) materials also purchased from Sigma Aldrich. Here, for the formulation of the desired SC inks, three compatible solvents anisole, dimethyl sulfoxide, and water with concentration from 30 µg mL⁻¹ to 3 mg mL⁻¹ were evaluated. The solid SCs were set to dissolve in the respective solvents within a period of 0.5 h with temperature maintained at 30 °C. Among all, only anisole and water solvents were found suitable for formulating β-carotene and indigo inks, along with maximum solid content of 0.5 mg mL⁻¹. The inks that possessed best jetting capabilities along with the electronic properties are shown in Figure R2. Supporting Information, where the orange and purple colored inks contain β-carotene and indigo SCs, respectively.

Although, the jetting process of the PEDOT:PSS ink was already established in former research activities, jetting of the shellac, β-carotene, and indigo inks had to be optimized by adapting the jetting pulse waveforms within the software of DMP-2831 printer.[35] The deposition parameters for printing and curing the functional layers, and their device stack are shown in Table 2. In general, it is noted that the curing of the functional layers and devices was accomplished differently for capacitors and TFTs. For manufacturing capacitors, a total curing duration of 5 h was required for an entire batch of devices, whereas for TFTs, it would take up to 5.5 h. However, for both the devices, the process temperature had to be restricted to 60 °C, which is the maximum thermal capability of the biodegradable substrate Ormocere developed from Fraunhofer Institute for Silicate Research ISC in Würzburg, Germany. The substrate was mainly composed of polymer resins that get dissolved completely in contact with biological solution. The printed layers and devices were characterized physically, optically, and electrically using various measurement methods and equipments. The layer thickness and surface-related properties were studied using an optical microscope Zeiss Axios Observer M2m from Carl Zeiss Microscopy GmbH and Dektak 150 surface profilometer from Veeco Instruments Inc. The electrical properties such as the sheet resistance, capacitance (entirely measured at 10 kHz), current versus voltage characteristics for the printed functional layers and devices were evaluated using a PM5 probe station from Süss MicroTec, 2636A SYSTEM source-meter from Keithley and Agilent E4980A Precision inductance capacitance resistance (LCR) meter.

### 3. Results

The state-of-the-art inkjet-printed silver (Ag) layers are typically deposited on flexible polyethylene naphthalate (PEN) film, to obtain conductive structures contributing toward the development of electrodes for passive devices like resistors and capacitors or active devices like diodes and TFTs. For developing conductive electrodes that can be utilized for the applications in microelectronics, it is found crucial to achieve a sheet resistance below 1 Ω□⁻¹, along with desired pattern definition. In case of the Ag-based conductive layers, manufactured using inkjet technology, certain parameters, e.g., ink formulations and content (material either nanoparticle or solution based), pattern definition (width, length and thickness), printing (print-head, drop volume, resolution, and speed), and postprocess (sintering methodology and parameters) become the deciding factors for achieving the desired geometrical and electrical characteristics. The electrical sheet resistance of an inkjet-printed Ag layer can typically range about 1 ± 0.5 Ω□⁻¹ for thickness of 0.2–0.5 μm.[17]

In comparison to this, conductive polymers like PEDOT:PSS exhibit their conductivity on a different electronic basis, especially with the hoping charge transportation mechanism. Here, the interpolymeric morphology is very critical. Although, the conductivity of the printed PEDOT:PSS layers cannot match with the printed Ag layers, but it is moderate enough to allow charge transportation within the electrodes and allow charge accumulation at the dielectric and/or SC interfaces. As mentioned earlier, in this work, a commercially available PEDOT:PSS ink (Heraeus) was used for the printing of conductive layers. The deposition parameters for manufacturing the PEDOT:PSS layers were kept constant (shown in Table 2). The printed PEDOT:PSS layers were found to be uniformly distributed and the thickness varied in the range of 500 ± 50 nm. The electrical characteristics of the printed layers were evaluated using an LCR and source meter, where it was concluded, that when the geometry of the conductive tracks was varied, i.e., width between 0.5 and 2.5 mm and length between 5 and 20 mm, the terminal resistance varied from 60 to 850 Ω. In addition, the sheet resistance of printed layers with dimension 5 × 5 mm² and 0.5 μm thickness were measured using the four-point probe measurement method and concluded to vary in the range of 40 ± 5 Ω□⁻¹.[4]

Furthermore, deposition of an inkjet-printed dielectric layer based on polymeric material typically was found very challenging. The first main reason was the intrinsic electronic property of the addressed materials, and the second being occurrence of the physical irregularities of the printed layer from the deposition
process. Next to this, the printing and post-treatment process of a polymer-based dielectric ink is very challenging. Here, several optimization steps were executed in various aspects, e.g., generating optimal jetting parameters for inks having different formulations, obtaining homogeneity of the laid-down wet layer, and appropriate transformation of the printed layer from wet to solid state, while preventing the impact of the coffee ring effect. Finally, establishing the curing parameters for the dielectric including the expulsion of solvent from the layer, while keeping the physical integrity of the substrate unharmed.

As indicated in Section 2, for validating the physical–chemical stability and furthermore the jetting process, different inks were formulated based on the different shellac weight percentages with respect to the solvents. At first, optically the solubility of shellac was evaluated in different solvents (ethylene glycol, water–ethanol mixture, and PGMEA). It was observed that the most stable and compatible solvent for formulating the shellac dielectric ink was ethylene glycol. All the other ink formulations within 2 weeks showed irreversible effects, which were either material agglomeration or haziness. In Figure R3A, Supporting Information, two ink formulations (Ink A and Ink H) are shown that has the same material loading, i.e., 1 wt%, but different solvents, i.e., right bottle contains PGMEA while left bottle contains ethylene glycol. It can be clearly seen that Ink H shows solubility problems, whereas the one with ethylene glycol is dissolved easily. In comparison, all the other inks, i.e., Ink E–Ink J had the same solubility problems, that concluded that water–ethanol (1:1) and PGMEA were not suitable solvents for the shellac ink formulation. All the inks formulated with ethylene glycol with different shellac loadings shown in Figure R3B, Supporting Information, e.g., Ink A (1 wt%), Ink B (4 wt%), Ink C (7 wt%), and Ink D (10 wt%) were well qualified for the stability and jetting process. Out of these inks, Ink C demonstrated the best compromise of highest material loading and best jetting capability. The viscosity and surface tension properties of the most optimal shellac ink, i.e., “Ink C” (7 wt%), were measured at 25 °C with Rheometer Physika MCR Anton Paar and Krüss mobile drop, and were found to be 18 ± 2 mPas and 60 mN m⁻¹, respectively. To obtain a reliable jetting process for this high viscous ink, a much intensified waveform along with an elevated cartridge temperature of 50 °C was developed, that resulted into generation of drops without instability for a longer time scale.

The preliminary investigations were done by Mitra et al., where the deposition of the shellac dielectric ink by the inkjet printing process was shown possible for developing passive devices, e.g., capacitors. The shellac ink (Ink C with 7 wt%) being the preferred choice, showed an excellent ink jetting capability. But, the transformation of the deposited drops to form of a layer was found to be challenging. The ink was found to have relatively high surface tension (about 60 mN m⁻¹), which led to layer shrinkage and in-homogeneity. The deposition process was then optimized in such a way that there would exist a perfect harmony between the rate or volume of deposited ink with respect to a defined substrate temperature, allowing an optimal ink spread-out over the area of the printed layer. From the various print tests and consequent observations, a substrate temperature of 30 °C was found to be the best choice for achieving a continuous spread-out layer without defects (additional information regarding 40 and 60 °C substrate temperatures is available in the Supporting Information). When the substrate temperature was further increased, the layer started to shrink fast due to the inappropriate surface tension, resulting into discontinuity in the layer formation. Next to this, printing drop space of 10 μm (2540 dpi resolution) along with two layers were required to obtain a defect-free reliable insulating layer for further investigation. In Figure 2, microscopic images of the printed shellac layers on top of the already printed PEDOT:PSS layer are shown, where Figure 2A shows the layer discontinuity (10 μm drop space and 1 layer) located at the bottom left corner of the printed square, whereas, Figure 2B shows counteraction to this challenge with the deposition of a second layer, with the exception of the minor shrinkage occurring at the corner location. It was observed that in both conditions, there is existence of strong coffee ring effect. Although, the formation of the ring-shaped structure is much wider and thicker for the printed shellac layer constituting of two layers, the addressed print parameters were found reliable, as compared with the ones constituting of one layer. The main problem with the deposition of a single printed shellac layer is the emergence of defects (randomly distributed) in form of pinholes over the entire area of the layer, where the PEDOT:PSS layer is potentially exposed from the bottom side, thus creating electrical short circuits upon contact with the top electrode.

A representative surface topology of a printed shellac layer is shown in Figure 2C, where the cross-sectional profile of the layer was measured using a mechanical surface profilometer (10 measurements). The profile of the printed layer shows that, at the center of the shellac layer, the topology is uniform and the material is distributed homogenously with a thickness of ≈2.5 μm. On the contrary, the peaks at the edges of the layer could reach 15–30 μm. These irregularities caused due to the coffee ring effect were restricted to the location 2 mm away from the edge of the printed layer from all sides. For a better comparison, the thickness of the shellac dielectric was increased by implementing the printer’s highest resolution of 5080 dpi (5 μm drop space) along with one and two layers. Here, the layer thickness was noticed to vary 5.75 ± 1.25 μm, respectively. Due to the thermal stability limitation of the biodegradable Ormocere substrate, the curing for both the materials were restricted to 60 °C, with the exception of different curing durations, i.e., 1 h for PEDOT:PSS electrodes and 4 h for shellac dielectric in a vacuum oven. The optimized print parameters were implemented for depositing the PEDOT:PSS electrodes and shellac dielectric, to finally develop the capacitors (quantities up to 30).

As mentioned earlier, for evaluating the influence of the dielectric’s thickness to the electrical characteristics and reliability of the manufactured capacitors, several devices were printed using different parameters for the shellac dielectric, i.e., 1 layer with 5 μm drop space, 2 layers with 5 μm drop space, 1 layer with 10 μm drop space, and 2 layers with 10 μm drop space. The measured layer thicknesses corresponding to the varied drop spaces and number of layers are 4.5 ± 0.2, 6.5 ± 0.5, 1 ± 0.1, and 2.2 ± 0.5 μm, respectively. For performing a valid comparison, the active area of the capacitors was kept constant to 25 mm². Figure 3 shows four important aspects of the shellac dielectric. One of the main outcomes of the investigations is that, shellac could definitely be utilized as a dielectric material in form of printed thin films for manufacturing capacitors using inkjet
technology. Next to this, the graph also exhibits that as the dielectric’s thickness decreases from 7 to 1 μm, the capacitance increases from 100 to 300 pF with a dielectric constant of 3. During the measurement process, it was discovered that the highest manufacturing yield of 90% was only feasible with the dielectric composed of two printed layers (for both 5 and 10 μm drop spaces). Although, the printed capacitors manufactured using 1 layer with 10 μm drop space and 1 layer with 5 μm drop space showed the highest capacitance of about 275 and 250 pF, the manufacturing yield behind developing these devices was less than 30%. On the contrary, the capacitance obtained from the devices processed with 10 μm drop space and 2 layers resulted into 210 ± 50 pF, whereas the dielectric processed with 5 μm drop space and 2 layers could only offer 100 ± 10 pF. Hence, as conclusion, the former parameters (10 μm drop space and 2 layers) were considered as the best settings for achieving capacitors, with the most optimal electrical characteristics and manufacturing reliability. A series resistance of 5.25 × 10^8 Ω was measured for the capacitors that exhibited most stable characteristics. The value for the capacitor’s resistance is considered as high due to the thick dielectric layer, and second, due to the resistance offered by the PEDOT:PSS electrodes. As extension of the previous investigation, second set of the electrical measurements was carried out after 1 month, for the same functional capacitors. The main goal here was to research on the electrical degradation of the printed shellac dielectric corresponding to the capacitors, upon the exposure to the ambient atmosphere. A noticeable electrical degradation of the capacitor performance was expected, since the implemented shellac dielectric was not crosslinked (component absent in ink), and second, the devices should ideally possess the functionality to degrade with time. The second measurement set (marked with black bars) showed that all the devices were functional and the obtained capacitance for all the devices manufactured with different parameters was reduced by 15% only.

Additional tests were conducted to validate the degradation of printed shellac layer in a biological solution, which indicated that 48 h are required to dissociate shellac’s dielectric properties and generate leakage current. Investigation regarding the
disintegration was carried out, where the interaction between the printed shellac dielectric layer and sodium chloride (NaCl) solution was mainly focused. For the preparation of the samples, conductive interdigitated electrodes were first deposited on the biodegradable Ormocere substrate. Finally, on the active area of interdigitated electrodes, 3 μm-thick shellac layer was deposited using the most optimal printing and post-treatment parameters. Later on, these prepared samples were immersed in the NaCl solution, and then characterized for the electrical properties. The sample preparation and the measurement setup is shown in Figure 4A,B. In Figure 4C, the graph about the electrical characteristics of the immersed samples is shown, by the development of the leakage current with respect to time interval extended to 3000 min (48 h). During this measurement interval, it was seen that the leakage current started with a value more than 10 μA, and finally increased to several mA after completion of 48 h. This proves that during this time interval, the shellac layer undergoes degradation with interaction to NaCl solution and thus loses all its dielectric properties.

A successful process establishment of the printed capacitors ideally represented the development of functional building blocks for manufacturing printed TFTs. For manufacturing TFTs, a stack based on bottom gate bottom contact (BGBC) device architecture including four layers was adapted. The entire deposition of all the functional layers was accomplished on the same biodegradable Ormocere substrate. The bottom gate electrode (G) and interdigitated S/D electrodes were printed with PEDOT:PSS ink, along with the optimal deposition settings implemented while manufacturing the capacitors. Furthermore, the intermediate dielectric layer based on shellac was deposited using 10 μm drop space along with two layers, while keeping all the other settings fixed. The dielectric pattern was designed and positioned precisely above the active area of the G, which was followed by the deposition of S/D. The printing of S/D electrodes was considered as extremely critical, because of the required high positioning accuracy of the drops to generate the individual finger electrodes, that were spaced about 30 μm apart (channel length). The length of the S/D electrodes (channel width) was set to 1 mm and thus the effective calculated channel width-to-length ratio (W/L) was 30. These details are furthermore shown in Figure 5.

The optical microscopy of the printed PEDOT:PSS-based S/D electrodes show a slight ink bulging characteristics at certain locations. These bulges at various locations might potentially be the result of inappropriate ink spreading with respect to high ink deposition rate and volume. One of the main electrical requirements of G and S/D electrodes has always been the conductivity, which in turn is affected by the layer thickness or printing resolution. To keep consistency, the resolution of the S/D was kept constant, and that’s why counteracting the prevailing problem was momentarily suppressed. In Figure 5B, one can see a lot of particles distributed around the printed PEDOT:PSS G and S/D electrode layers. These are mainly the dust particles sticking on the opposite side of the fragile Ormocere substrate, which particularly accumulate, when Ormocere is initially supported by the PEN substrate for mechanical stability. The use of PEN support facilitates

**Figure 4.** Photographs of the prepared samples A,B) containing printed shellac layer deposited on the Ormocere substrate for the purpose of measuring degradation and C) graph representing the electrical leakage characteristics versus time interval.
batchwise execution of multiple printing and curing process steps, for the development of the entire device stack.

Once the deposition of G, dielectric, and S/D layers are accomplished with the corresponding post-treatments, deposition of the biodegradable SCs, i.e., β-carotene and indigo was carried out using inkjet printing. The pattern for the SC was arranged such that it would position itself exactly on top of the S/D electrodes. The printing of the SC as the last layer was found to be very straightforward and the related details regarding the ink formulations and implemented deposition parameters is shown in Table 2, in Section 2. As shown visually in Figure 5, 24 (2 × 12) TFTs were inkjet printed within two batches, fabricated with the fixed set of parameters. The only difference among the batch of 12 individual devices was the deposition of the two SCs, i.e., β-carotene and indigo. During the electrical evaluation of the TFTs, it was recognized that the manufacturing process yield for both the batches were different. It was observed that out of 12 devices with β-carotene as SC, the number of functional TFTs was only 4, which resulted into manufacturing process yield of 30%. Whereas, the manufacturing process yield for the TFTs with indigo SC was found to be ≈66%, corresponding to eight functional devices. This difference in the manufacturing yield can occur due to the occurrence of irregularity in layer interfaces, especially at the interface of the shellac dielectric, PEDOT:PSS S/D and β-carotene SC. Although, the solvents from the individual layers were extracted completely by the prolonged thermal curing process, the materials e.g., shellac (not cross-linked) and PEDOT:PSS still prone to get damaged upon the interaction of β-carotene ink containing anisole as solvent. In contrast, the water-based indigo ink formulation has a relatively mild interaction with the same materials, which lets the functional interface to hold the electrical integrity. This is because, first, the printed PEDOT:PSS layer is relatively thick ≈0.5 μm, which will not dramatically be affected by the water-based indigo SC ink, when deposited in low quantities. Second, the process of inkjet printing is controlled, by the application of substrate temperature and low deposition dosage of material, i.e., utilization of the limited print pitch during the deposition process and advancement of the SC pattern. Hence, the water content in the ink has higher chance to evaporate faster during the printing process. The output characteristics of the printed TFTs with the two SCs are shown in Figure 6, where Figure 6A,B corresponds to β-carotene and Figure 6C,D to indigo. The reason behind showing two output characteristics for each SC is to demonstrate the potentially expected performance regime from the printed TFTs with W/L = 30, defined material stack, BGBC architecture and specified geometry. In general, it is observed from the output curves, that the electrical performance of the TFTs obtained from indigo is better than β-carotene. It can also be observed that the TFTs with β-carotene SC show p-type characteristics, whereas the ones with indigo shows n-type characteristics. The electrical characterization process always includes voltage (V_DS) biased across S/D electrodes, thereby obtaining the corresponding current (I_DS), for a fixed voltage applied at the G electrode (V_GS). For this specific electrical measurement setup, TFTs were biased with V_DS ranging from 0 to 40 V and V_GS varied from 0 to 30 V (β-carotene) and 0 to 20 V (indigo), always with an increment of 5 V. From the electrical characteristics, it was concluded that during the operation of the TFTs both the typical linearity and saturation of I_DS can be achieved. For the TFTs with β-carotene, the linear and saturation regimes can be observed in the V_DS regimes between 0 and 15 V and above 15 V, respectively. On the contrary, the linear and saturation regimes lay differently for the TFTs with indigo, which is between 0 and 25 V and above 30 V, respectively.
A maximum driving $I_{DS}$ of 0.18 and 5 $\mu$A is achievable from the TFTs manufactured with $\beta$-carotene and indigo SCs, respectively. The electrical-dependent modulation of $I_{DS}$ to $V_{GS}$ is also considered as strong, as the current follows always a trend upon the change in voltage for both the SCs and all the functional TFTs. In addition, the field effect mobility at saturation regime was measured and found as $6 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for $\beta$-carotene and $7 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ for indigo SCs.

4. Conclusion

The research presented here can be summarized as a very novel work, which contributes toward the development of biodegradable microelectronic devices with defined performance, manufactured at 60 °C completely under ambient condition. The printed devices can be implemented potentially for actuation, testing and stimulation functions in the application fields of medical implants, health care, and recovery/rehabilitation. From the beginning, materials were selectively chosen, e.g., Ormocere substrate, PEDOT:PSS conductors, shellac dielectrics, and $\beta$-carotene or indigo SCs, for the layer buildup of an entire device stack for passive and active electrical components using inkjet technology. Although, PEDOT:PSS ink was commercially procured and implemented for developing the electrodes, other formulations containing degradable materials (dielectric and SC inks) were formulated in-house and made eligible for the inkjet technology. Furthermore, to achieve fully functional layers and devices, several parameter optimizations with regards to printing and curing of biodegradable and partially degradable inks were evaluated and then finalized. The material shellac was found as a high potential candidate for developing inkjet-printed dielectrics with $\approx 10$ pF mm$^{-2}$ capacitance, applicable for capacitors and TFTs. Next to this, $\beta$-carotene and indigo, both SCs along with the shellac dielectric and PEDOT:PSS electrodes were found appropriate for the development of inkjet-printed TFTs with full biodegradable and partial degradation capabilities. In total, the printed TFTs offer output currents between 0.18 and 5 $\mu$A and field effect mobility in the range of $6 \times 10^{-2}$–$7 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, upon the maximum operational voltage of 40 V. The printed devices realized using $\beta$-carotene and indigo SCs, show very different but typical characteristics, which will let them get utilized for the development of switching or complimentary circuits in function of p- and n-type electrical properties.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.
[49] R. Tong, G. Chen, J. Tian, M. He, Carbohydr. Polym. 2020, 227, 115366.
[50] M. A. U. Khalid, M. Ali, A. M. Soomro, S. W. Kim, H. B. Kim, B.-G. Lee, K. H. Choi, Sens. Actuators A: Phys. 2019, 294, 140.
[51] E. J. Curry, K. Ke, M. T. Chorsi, K. S. Wrobel, A. N. Miller, A. Patel, I. Kim, J. Feng, L. Yue, Q. Wu, C.-L. Kuo, K. W.-H. Lo, C. T. Laurencin, H. Illies, P. K. Purohit, T. D. Nguyen, Proc. Natl. Acad. Sci. 2018, 115, 909.
[52] D. She, M. Tsang, M. Allen, Biomed. Microdevices 2019, 21, 17.
[53] H. Lee, G. Lee, J. Yun, K. Keum, S. Y. Hong, C. Song, J. W. Kim, J. H. Lee, S. Y. Oh, D. S. Kim, M. S. Kim, J. S. Ha, Chem. Eng. J. 2019, 366, 62.
[54] A. A. La Mattina, S. Mariani, G. Barillaro, Adv. Sci. Rev. 2020, 7, 1902872.
[55] K. Y. Mitra, A. Willert, A. Sossalla, M. Hoffmann, R. Zichner, in Proc. in 22nd European Microelectronics and Packaging Conf. & Exhibition, IEEE, Pisa 2019, pp. 1–8.