Additive manufacturing for printed electronics and integrated systems

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XXXII Cycle

Valentina Bertana

Supervisor: Prof. Luciano Scaltrito

Research context and motivation

The proposed research activity can be divided into two main branches, with 3D printing as common denominator: **doped polymers** and **miniaturized devices**. The first is about the development of new materials in order to add functionalities to the printed objects (e.g. electrical conductivity). The latter concerns the study of miniaturized devices for micro- /nano- particles separation.

During the first PhD year, research activities were mainly focused on the doping of polymers with conductive fillers and the optimization of printing processes at different scale for miniaturized devices. As regards the doping of polymers, new tests during the second PhD year led to the preparation of an electrically conductive poly(3,4-ethylenedioxythiophene) (PEDOT) resin for stereolithography. As regards miniaturized devices, a prototype of a microscopic filter was produced and characterized before the scaling to the nano-dimensions, aiming to overcome the drawbacks of the horizontal filtering device developed during the first PhD year. In the last PhD year the research activity has been addressed to the integration of 3D printed conductive PEDOT parts inside an electric circuit. Thus, printed devices containing PEDOT, e.g. organic electrochemical transistors (OECTs) employed as biosensors, could be effectively integrated in a more complex system, e.g. Lab-On-a-Chip (LOC). Moreover, the previously developed resin containing silver nanoparticles, whose electrical conductivity value was too low to be exploited as conductive 3D printing resin, was declined in resin for 3D printing of antibacterial devices.

Addressed research questions/problems

- **Doped polymers**
  - **PEDOT resin:** The preparation of the PEGDA/PEDOT resin was revised in order to obtain a stable dispersion of PEDOT inside PEGDA and to reduce the PEDOT flake dimension, thus overcoming printing accuracy issues not caused by the printer. Then, metal plating techniques were investigated to allow for PEDOT parts to be inserted in a more standard circuitry.
  - **Silver nanoparticles (Ag NPs) resin:** The resin containing silver salts (to be converted in silver nanoparticles) was employed to print objects with Ag NPs patterns. Then, patterns generated with different parameters were tested to assess the possibility of printing miniaturized devices with antibacterial properties.
- **Miniaturized devices**

  The filtering device reported in the paper "A passive two-way microfluidic device for low volume blood-plasma separation" was furtherly tested with smaller particles (< 1 µm) and showed encouraging results. But an improvement was needed since three of the five device channels had filling issues (Fig.1).

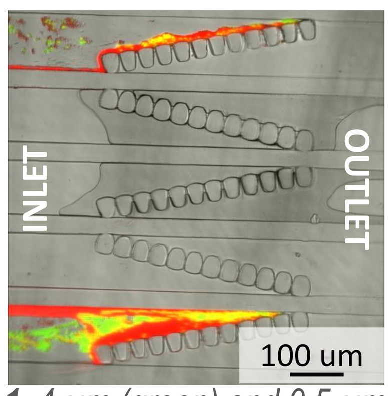

Figure 1. 4 µm (green) and 0.5 µm (red) FluoSpheres blocked by the filter. The three central channels showing filling issues

Adopted methodologies

- **Doped polymers**
  - **PEDOT resin:** PEDOT flakes extracted from Clevios were reduced to nanometric size with a sonifier (Branson SFX250) at 70% power for 10 minutes. Then, a resin containing PEGDA and PEDOT at 35% wt. was prepared and employed in the Microla SL printer. Printing parameters were 15 mW nominal laser power, 2000 mm/s laser velocity. OECTs with a 700 µm wide channel were printed to assess printing accuracy. PEDOT parts were metal plated with silver paste (RS Pro), gold sputtering (Q150T-ES Quorum Technologies) and copper electroplating (electrolyte solution-TECHNI CU 2300 RTU, Italgalvano S.p.a). The specimens where then electrically characterized by a two-point measurement, setting the voltage from -1V to +1V and reading current values (Keithley 6430 Cleveland, OH).
  - **Silver nanoparticles (Ag NPs) resin:** squared samples were printed, and then Ag NPs line patterns generated by Microla SL printer in the same process. The conversion from Ag salts ($AgNO_3$) to Ag NPs was performed with 30 mW nominal laser power and 1 mm/s scan velocity, scanning twice. Line patterns with decreasing hatch spacing (0.08 mm, 0.04 mm, 0.02 mm) were considered. The samples were then immersed in a solution containing sea bacteria, and bacteria viability evaluated at different times by UV-vis spectroscopy (LAMBDA 950) .
- **Miniaturized devices**

  A new filter configuration was proposed and a master for polymeric replicas fabricated via standard cleanroom processes. A soda lime mask was prepared, then lithography on a silicon wafer with resist mask performed. Silicon was then etched by RIE process and the mask removed in an acetone bath.

Novel contributions

- **Doped polymers**
  - **PEDOT resin:**

    The new resin allowed for the precise printing of a 700 µm wide OECT channel (Fig. 2). Electrical characterization of metal plated PEDOT samples showed that copper electroplating produces an even copper layer which allows for a proper electrical connection and a reduced probe contact resistance (Fig. 3).

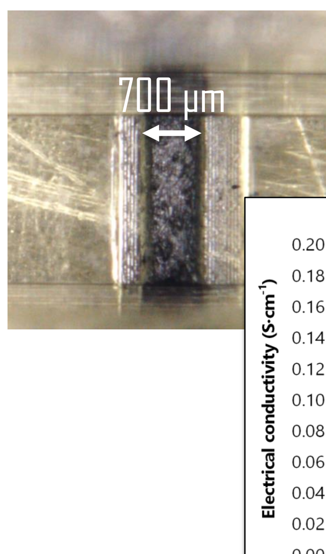

Figure 2. 3Dprinted OECT channel

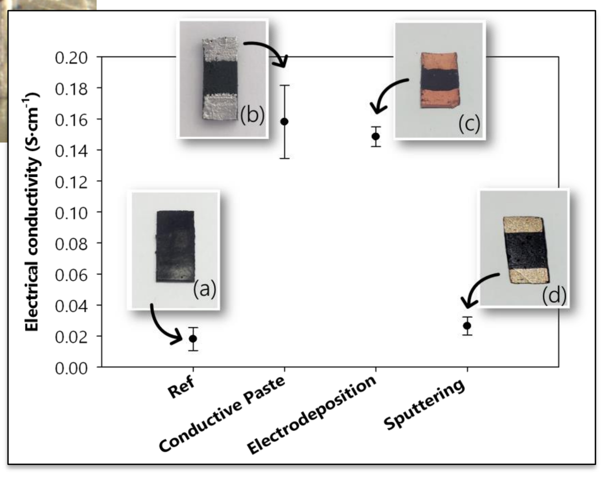

Figure 3. Results from conductivity tests

  - **Silver nanoparticles (Ag NPs) resin:**

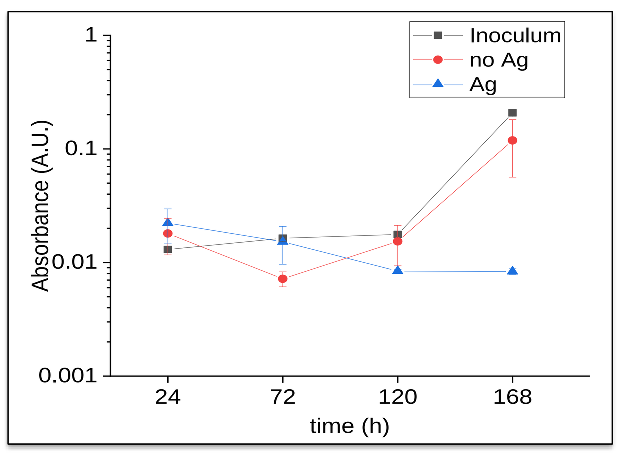

Figure 4. Results from antibacterial tests

UV-vis tests have demonstrated that, the more the generated silver nanoparticles, the more the antibacterial effect. Since live bacteria membrane absorbs light, a reduced absorbance means reduced viability (Fig. 4)

- **Miniaturized devices**

  Fluorescence filtration tests have not yet been performed, but it is expected that a silicon master with a resolution of c.a.2 µm (Fig. 5) will produce a device with filtering capabilities down to few hundreds nanometers.

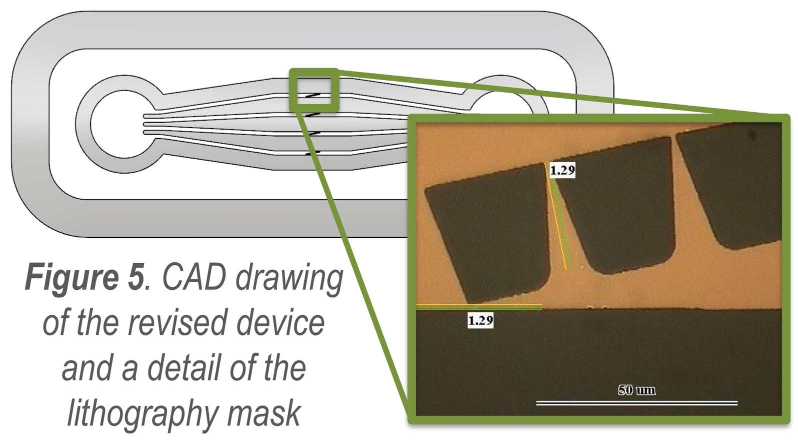

Figure 5. CAD drawing of the revised device and a detail of the lithography mask

Future work

Next steps in the proposed research topic will be moved towards the additive manufacturing of a complete LOC, including the sample preparation (filtration) and the sensor (OECT), everything integrated in a standard electric circuit for LOC control and data acquisition.

Submitted and published works

- G. Gonzalez, V. Bertana, et al., Development of 3D printable formulations containing CNT with enhanced electrical properties, Polymer. 109 (2017) 246–253. https://doi.org/10.1016/j.polymer.2016.12.051 (Published)
- V. Bertana, C. Potrich, et al., 3D printed microfluidics on thin Poly(methyl methacrylate) substrates for genetic applications, Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena 36, 01A106 (2018), https://doi.org/10.1116/1.5003203 (Published)
- S.L. Marasso, V.Bertana et al., PLA conductive filament for 3D printed smart objects, Rapid Prototyping Journal, Vol. 24 Issue: 4, pp.739-743, https://doi.org/10.1108/RPJ-09-2016-0150 (Published)
- G. De Pasquale, V. Bertana, L. Scaltrito, Experimental evaluation of mechanical properties repeatability of SLA polymers for labs-on-chip and bio-MEMS, Microsyst Technol (2018) 24: 3487. https://doi.org/10.1007/s00542-018-3753-1 (Published)
- F. Perrucci, V. Bertana, et al., Optimization of a suspended two photon polymerized microfluidic filtration system, Microelectronic Engineering, Volume 195, 2018, Pages 95-100, https://doi.org/10.1016/j.mee.2018.04.001 (Published)
- A. Massaccesi, V. Bertana et al., 3D-Printable DielectricTransmitarray With Enhanced Bandwidth at Millimeter-Waves, IEEE Access, vol. 6, pp. 46407-46418, (2018). https://doi.org/10.1109/ACCESS.2018.2865353 (Published)
- G. Scordo, V. Bertana et al. A novel highly electrically conductive composite resin for stereolithography. Mater Today Commun. 2019 Jun;19(September 2018) Pages 12–7. https://doi.org/10.1016/j.mtcomm.2018.12.017 (Published)
- V. Bertana,G. De Pasquale et al. 3D Printing with the Commercial UV-Curable Standard Blend Resin: Optimized Process Parameters towards the Fabrication of Tiny Functional Parts. Polymers (Basel). 2019;11(2):292. https://doi.org/10.3390/polym11020292 (Published)
- G De Pasquale, V. Bertana et al. Numerical and experimental evaluation of SLA polymers adhesion for innovative bio-MEMS. Mater Today Proc. 2019 Volume. 7 Pages 572–7. https://doi.org/10.1016/j.matpr.2018.12.010 (Published)
- L. Spigarelli, V. Bertana et al. A passive two-way microfluidic device for low volume blood-plasma separation. Microelectron Eng. 2019 Issue Mar;209(February) Pages 28–34. https://doi.org/10.1016/j.mee.2019.02.011 (Published)
- G. Tarabella G, V. Bertana et al. Multifunctional Operation of an Organic Device with Three-Dimensional Architecture. Materials (Basel) 2019 Apr 25;12(8):1357. https://www.mdpi.com/1996-1944/12/8/1357 (Published)
- A. Massaccesi, V. Bertana et al. Broadband Dielectric Transmitarray with Scanning Capabilities. In: 2019 13th European Conference on Antennas and Propagation (EuCAP). 2019 ISSN 2164-3342 (Published)

List of attended classes

- 02RHPRV - Intellectual Property Rights, Technology Transfer and Hi-tech Entrepreneurship (23/3/2017, 40)
- 01QORRV - Writing Scientific Papers in English (8/6/2017, 20)
- 01MOUKI - Materiali polimerici nanocompositi (21/4/2017, 33.33)
- 04NPEPE - Materials for MEMS and characterizations of technological processes (30/1/2017, 83.33)
- 01NPOPE - Micro and nanotechnologies applied to biomedicine, environment and energy (8/2/2017, 100)
- 01QFDRV - Photonics: a key enabling technology for engineering applications (24/7/2017, 41.67)
- 01NYCPE - Physics of technological processes for Micro & Nano systems (17/7/2017, 100)
- 01MOVKI - Polimeri e radiazioni (16/2/2018, 33.33)
- Basic Vacuum Course -AIV XXIII Conference -Firenze(4/4/2017, 4)
- Short courses of the MNE Conference, September 2017 – Braga, Portugal (27/8/2018, 8)
- International School on Graphics and Geometry Processing for Digital Manufaturing – Brescia (18/10/2018, 20)