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ALL-POLYMER MICROELECTRODE FABRICATION VIA HIGH-THROUGHPUT SOFT EMBOSSING

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The demand for low cost and fast processing microelectrodes devices is pushing industry to search alternatives to the standard solid state technology. In this context the use of conducting polymers is an appealing option for the development of new organic devices [1]. In particular, the interest in the use of conductive polymers is rapidly increasing for the development of wearable devices with applications that require biocompatibility, flexibility and low cost such as sports performance sensors, military healthcare applications and Poly(3,4-[2]. thylenedioxythiophene) (PEDOT) is one of the most used conductive polymers thanks to its advantageous properties [3] such as the high transparency, ease in film processing and a tunable conductivity that can be increased by composite doping (with for example Dimethyl sulfoxide and Carbon Nanotubes) or by treatment with acids (such as H₃PO₄) [4]. PEDOT can be patterned in order to create microelectrodes by means of in situ electropolymerization, inject-printing techniques, laser ablation and hot embossing [5]. However, all these methods suffer from several drawbacks such as long fabrication times and high costs. An interesting approach is a soft embossing process which differs from a standard hot embossing process in the use of polymeric embossing stamps instead of hard aluminum or silicon materials [6]. This approach drastically reduces the production costs and renders the process easy to scale up and be automated.

Here we present a soft embossing process that allows the manufacturing of microelectrodes on a flexible polymeric foil with a simple and low cost process. The technology is the basis for the development of an all-polymer wearable device for pH monitoring during chronic wound healing. Indeed, acidification is one of the key indicators of infection [7], and yet a wearable, low cost device for wound pH monitoring is still missing on the market.

The first step in microelectrodes manufacturing is the fabrication of a soft working stamp from a patterned silicon master. This process can be repeated many times obtaining several soft working stamps from a single hard stamp, lowering the fabrication costs. An antistiction layer (Methyl nonafluorobutyl ether + Methyl nonafluoroisobutyl ether) is spin coated (2000rpm) on the patterned silicon master and baked for 10min at 120°C. The polymer used as working stamp is MD700 (perfluoropolyether (PFPE)-urethane dimethacrylate) mixed with a photoinitiator (Igracur 2022). The MD700 polymer is cast between the patterned silicon master and a glass wafer and it is cured for 200s in UV light. The cured polymer adheres to the glass wafer and can be directly used as soft working stamp without the need of an antistiction layer thanks to the low surface tension of MD700. The substrate for the embossing is a bilayer made of a a thermoplastic cyclic olefin copolymer (COC) foil (300 µm thick TOPAS® foil with glass transition temperature equal to 70°C) and a thin layer of a conductive polymer (PEDOT). After cleaning with ethanol and air plasma (5 minutes at 60W), the COC foil is covered with the PEDOT layer by means of a spin coating process at 1000rpm for 60s. The resulting thickness of the PEDOT layer was measured with a profilometer and it is equal to (135 ± 7) nm. The conductivity of the PEDOT layer has been evaluated by means of 4-point probe measurements. The result is shown in figure 1 (black squares) where the voltage response is plotted as a function of the applied current. The linear fit allows to obtain the electrical resistance and to calculate the conductivity of the

film, which is 0,6 S/cm.



Fig. 1: Current-Voltage curves obtained with 4-point probe measurements on the PEDOT layer before (square) and after (dots) the treatment with H_3PO_4 .

In order to increase the conductivity, the PEDOT was immersed for 3 minutes in H_3PO_4 . The electrical response of the film after the treatment is plotted in figure 1 (grey dots). The electrical resistance decreases consistently leading to an conductivity equal to about 10 S/cm.

The embossing process was carried out by placing the soft working stamp against the substrate. The embossing temperature was set to 90°C, the pressure was set to 6000N for 3 minutes and the releasing temperature was set to 50°C. The embossing process was performed with a working stamp patterned with lines of different dimensions and spacing. The evaluation of the imprinted structures was performed with an optical interferometer.



Fig. 2: Interferometric image of the imprinted PEDOT-COC sample. Lines 5 µm wide, 300nm high. Spacing 5 µm.

An example of the imprinted structures is shown in the interferometric image of figure 2 (lines $5\mu m$ wide, 300nm high separated with $5\mu m$ spacing). The reproducibility of the pattern is excellent in the range between $1\mu m$ and $10\mu m$ of lateral dimension, yielding an identical pattern transfer.

In conclusion, we have implemented a fast, low cost and high throughput procedure for micropatterning a patterned layer of conductive polymer (PEDOT) by means of a soft embossing process. Moreover, we have also found a fast post-manufacturing treatment to increase the conductivity more than 10 fold. These results are the basis for the realization of a wearable microelectrodes device for pH monitoring during wound healing.

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