Thin Solid Films 636 (2017) 438–445

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Metallization and electrical characterization of platinum thin film microelectrodes on biocompatible polydimethylsiloxane substrates for neural implants

María del Carmen Fuentes [a,b,*], Noemí Pérez [a,b], Isabel Ayerdi [a,b]

[a] Ceit-IK4, Paseo de Manuel Lardizábal, 15, 20018 Donostia – San Sebastián, Spain
[b] TECNUN - Universidad de Navarra, Paseo de Manuel Lardizábal, 13, 20018 Donostia – San Sebastián, Spain

ARTICLE INFO

Article history:
Received 19 November 2016
Received in revised form 6 June 2017
Accepted 8 June 2017
Available online 8 June 2017

Keywords:
Polydimethylsiloxane
Flexible structures
Microelectrodes
Platinum

ABSTRACT

Microfabrication technology in the biomedical field has provided microelectrode arrays for neural implants with new development opportunities. The need for more complex physiological functions and miniaturization, as well as the use of new materials for more flexible electrodes, can now be satisfied. PDMS (Polydimethylsiloxane) substrates are elastic, biocompatible and permeable to oxygen, in addition to being a highly stable material. However, the implementation of microfabrication techniques such as deposition and patterning processes on these new substrates is not straightforward. This paper will describe the development of a reliable method to metalize thin film microelectrodes on a highly flexible medical grade PDMS layer that is suitable for long-term implantation. Platinum (Pt) microelectrodes were deposited by physical vapor deposition and pattern transfer by lift-off was chosen. Standard photolithography was used to pattern a conventional positive photoresist and was optimized to improve adhesion and to avoid cracks in the resist. The electrical behavior of the metal-polymer interface was analyzed using multiplexed DC measurements. The resistance values of seven samples and a control were acquired sequentially. Special attention was paid to the connectorization from the flexible microelectrodes to a rigid substrate. Measurements were carried out in an air-protected environment as well as in a biological environment designed to mimic the environment of the human body. Long-term stability of the Pt-PDMS interface was strongly influenced by the electrode configuration and its connection. A characteristic electrical behavior was observed for a straight-electrode configuration. This configuration demonstrated significant drift of resistance values of more than 4% during the initial 56 h. By contrast, a stable behavior was observed for a loop electrode design, with only small variations of less than ±0.5% caused by thermal fluctuations.

1. Introduction

Microfabrication techniques have been widely used for metallization in industry and research. Thin film deposition and pattern transfer techniques have been applied for decades to pattern electrodes in the micron range. Integrated circuit (IC) and microelectromechanical systems (MEMS) technologies have used these well-established techniques to fabricate reliable conductive geometries on rigid substrates. However, the emergence of flexible materials for ICs and (Bio)MEMS has created the need for reliable metallization on flexible substrates.

In the last decade, many MEMS-based thin film microelectrodes have also been proposed for neural interfaces for stimulation and recording purposes [1,2]. From a technological point of view, the advantage in using flexible polymers as substrate in biomedical applications over rigid materials such as silicon lies in their lower Young's modulus. Flexible substrates result in more compliant and softer microelectrodes and, therefore, establish a better match with the mechanical properties of soft biological tissue. Flexible microelectrodes based on parylene, polydimethylsiloxane (PDMS) and polyimide have been developed for biomedical applications using microfabrication techniques [1,3,4]. However, despite all the work already done in this field, the implementation of metal deposition and patterning processes on PDMS substrates are not straightforward. Adhesion problems between photosensitive materials or metal layers and PDMS substrates have been reported [5]. And although various methods, including chemical and plasma treatments [6–8] have been proposed to improve adhesion, no standard approach has been established. The best option strongly depends on the individual properties of the PDMS used. Therefore, a fabrication process that achieves reliable metallization must be developed for each specific PDMS according to the needs of the specific application. Various methods are described to pattern metal thin film on the commonly used PDMS, Sylgard 184 from Dow Corning [9,10,11,12,13]. However,

* Corresponding author at: Ceit-IK4, Paseo de Manuel Lardizábal, 15, 20018 Donostia – San Sebastián, Spain.
E-mail address: mariadelcarmen.fuentes@gmail.com (M.C. Fuentes).

http://dx.doi.org/10.1016/j.tsf.2017.06.017
0040-6090/

this PDMS is not suitable for long-term implantation. So, in the case of microelectrodes for neural implants, a new process development is required for metallization on biocompatible medical grade PDMS substrates that meet standards for implanted medical devices.

The introduction of biocompatible soft microelectrodes also needs to provide stable and reliable interfaces. Many polymer-based microelectrodes have been developed for biomedical applications in research. Momentary impedance measurements have been described for flexible gold microelectrodes based on PDMS showing comparable values to rigid microelectrodes [12]. In that work, the PDMS Sylgard 184 was used to produce a 70 μm – thick layer as the electrode carrier. Other studies show similar behavior for metal patterns on polyimide substrates [11,14]. Still others have measured impedances as a function of mechanical deformation for gold patterns on parylene layers under cyclic stretching and bending [16] and for gold patterns on polyimide under uniaxial strain [11]. Long-term stability of Pt/Au electrodes fabricated on PDMS, parylene-deposited PDMS and parylene-caulked PDMS has been reported [15]. This work shows a decrease in impedance over time with a slower impedance change for parylene-caulked PDMS compared to PDMS only. Long-term impedance changes have also been measured for gold patterns on parylene layers [16]. However, measurement of electrical long-term stability has not been reported for PDMS-based Pt only microelectrodes.

In this work, we developed a reliable metallization process for microelectrodes embedded in flexible, stretchable and biocompatible PDMS layers suited for long-term implantation. The highly flexible medical grade MED-4011 PDMS was chosen as it matches the mechanical compliance of biological tissue better than other flexible substrates (e.g. parylene and polyimide) and would minimize potential mechanical interactions and tissue damage during implantation. Microfabrication technology was proposed to develop platinum (Pt) microelectrodes. Pt is commonly used as electrode material for stimulation electrodes because of its excellent corrosion resistance and safe stimulation charge density in chronic stimulation applications. An optimized photolithographic process and a lift-off technique were used for patterning a Pt thin film deposited by sputtering. In addition, the electrical behavior of the metal-polymer interface was analyzed by multiplexed DC measurements. In the context of electrical measurements, the connectorization of the flexible samples to the measurement system is a major difficulty. Therefore, special attention was paid to the electrode configuration and external connection. Measurements were carried out in an air-protected environment and in physiological saline solution in order to simulate a biological environment such as would be present in the human body.

2. Methods

2.1. PDMS-based microelectrodes

MEMS manufacturing processes were proposed for the fabrication of thin film microelectrodes based on PDMS microlayers. Samples for electrical characterization consisted of a base polymeric layer, a single electrode layer and a passivation layer with a total thickness of 300 μm. The electrical behavior of the metal-polymer interface was measured under laboratory conditions with two different electrode configurations (see Fig. 1):

- *Straight-Trace Electrodes* were rectangular samples (40 mm × 0.7 mm) featuring a straight mono-electrode configuration as the metal layer. The two contact pads (5 mm × 0.7 mm) were on opposite ends. Electrode traces of 0.3 mm in width were considered (Fig. 1a).
- *Loop Electrodes* were non-rectangular samples with a 40-mm total length and a loop mono-electrode configuration as the metal layer. The two contact pads (10 mm × 2 mm) were located on the same end. Electrode widths of 0.1 mm and 0.2 mm were considered (Fig. 1b).

2.2. Electrode carrier

The silicone elastomer MED-4011, a medical grade PDMS from NuSil Technology suitable for long-term implantation, was chosen as the flexible substrate. A 270 μm-thick base layer was used as the electrode carrier. A SU-8 mould, photolithographically defined on a glass wafer, was used to obtain the thick PDMS layer (see Fig. 2a). The two-component silicone was mixed and poured into the mould for curing on a hot plate (Heidolph Hg 3001K, Sigma-Aldrich) at 150 °C for 1 h (see Fig. 2b).

2.3. Pt microelectrodes

Microfabrication techniques were used to comply with the dimensional requirements of the Pt microelectrodes. The definition of Pt microelectrodes on the electrode carrier involved three main steps: Photolithographic patterning of a photoresist on the PDMS substrate (see Fig. 2c), DC sputtering of a Pt layer (see Fig. 2d) and patterning of the Pt thin film by lift-off (see Fig. 2d).

2.3.1. Photolithographic patterning on PDMS microlayers

Standard photolithography was used to pattern the resist. The process steps were optimized to improve adhesion between the photoresist and the PDMS microlayer as well as to minimize mechanical stress and to avoid cracks in the resist layer. The substrate had to undergo a basic cleaning procedure and a dehydration step before the photolithographic process could be performed.

First, the PDMS microlayer was cleaned in ethanol and cleared in deionized water. Next the dehydration step removed the remaining water on the PDMS surface by placing the PDMS on a hotplate (Fisher Scientific™ Isotemp™ from Thermo Fischer Scientific) at 100 °C for 5 min. The wafer was, then, removed from the hotplate and allowed to cool for 1 min, during which care was taken to prevent any contact with any cool metal surface. The PDMS layer was then spin coated with Micro posit™ S1818™ G2 photo resist, manufactured by Rohm and Haas Electronic Materials. The photoresist was applied while the PDMS substrate

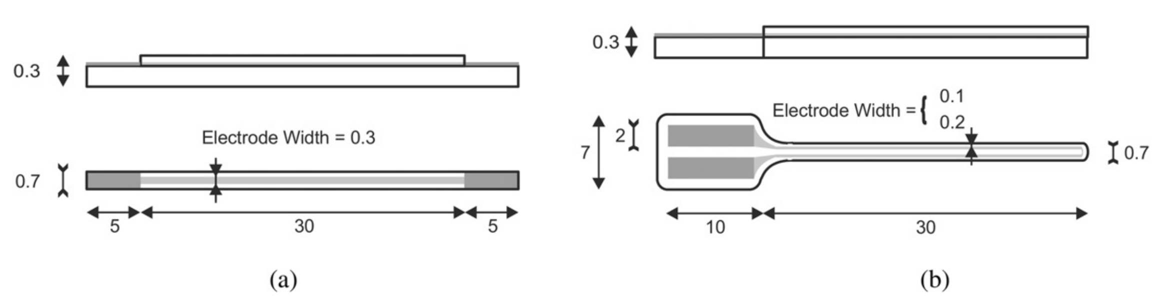

Fig. 1. Details of the platinum layer of the flexible microelectrodes. a) Straight-trace electrode with a rectangular shape and a straight mono-electrode configuration with an electrode width of 300 μm and the contact pads on opposite ends. b) Loop electrode with a non-rectangular shape and a loop electrode configuration with two different electrode widths and contact pads on the same end. Dimensions in [mm].