Microelectronic Engineering 133 (2015) 36–44

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Short Note

Electrical impedance, electrochemistry, mechanical stiffness, and hardness tunability in glassy carbon MEMS μECoG electrodes

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ARTICLE INFO

Article history:
Received 8 October 2014
Accepted 15 November 2014
Available online 22 November 2014

Keywords:
Neural probes
Implant
Microelectrodes
Glassy carbon
MEMS
Impedance matching

ABSTRACT

We report on electrical, electrochemical, mechanical stiffness, and hardness tunability of patternable glassy carbon (GC) microelectrodes for applications in bio-electrical signal recording and stimulation. Results from *in vivo* testing of a novel μECoG GC microelectrode array with beta activity recording of stimulation signals and their power spectra is reported, demonstrating a quantifiable superior performance of these electrodes as compared to metal electrodes. The microelectrodes – made from lithographically patterned and subsequently pyrolyzed polymer precursor – have excellent electrochemical stability in ionic solutions and respond well to chemical surface property modifications. In addition, lithographically patternable GC offers a unique tailorability functionality that enables fabrication of electrodes with a range of mechanical, electrical, and electrochemical properties that closely match the behavior of soft tissues. The pyrolysis conditions that drive this flexibility (i.e., maximum temperature, duration of pyrolysis, and ramp rate) could be varied to enable useful properties such as: (i) tailorable mechanical stiffness and hardness offering a much better stiffness-matching with soft tissues, (ii) tailorable electrical impedance for better impedance-matching with tissues, and (iii) tailorable electrochemical property useful for optimized stimulation and recording. We demonstrate that pyrolysis treatment at temperature of 1000 °C offers the most favorable electrochemical characteristics (least charge transfer resistance, most charge injection capacity, and decreased polarization resistance) and least impedance, whereas 800 °C results in maximum modulus of 55 GPa and hardness of 7 GPa. We, therefore, submit that these significant and original results reported here build a strong case for making GC microelectrodes, probes of choice for bio-signal sensing and stimulation applications, particularly for μECoG systems.

1. Introduction

There is an increasing research interest in interfacing microelectrodes with tissues for applications ranging from neural signal sensing and stimulation in BCI (brain–computer interface) for sensorimotor control, to chronic pain management and deep brain stimulation (DBS), among others [1–6]. In the specific area of neural probes, for example, substantial amount of research efforts over the past several years had concentrated in advances in single and array of neural electrodes capable of recording signals from the brain as well as stimulating specific brain regions [7,8]. These research efforts vary from those concentrating on stimulation and recording from a single neuron [9,10] to complex networks of neurons using multiple electrodes in cortical and sensory areas in brains [11–13]. For such probes, not only the architectures of the electrode structures, but also material properties are of major importance. Predictably, therefore, conventional and well-known materials that exhibit biocompatibility have been the traditional materials of choice. For instance, initial effort in neural probes employed glass tubes filled with electrolytes, where the glass acted as a biocompatible insulator [14]. Later developments involved single and arrayed metal wire electrodes that were manually assembled in an array format [15,16]. With MEMS (microelectromechanical systems) technology, however, microfabrication of micron-sized electrode arrays of variety of shapes using silicon, metal, and insulating and substrate materials such as polyimide have been made possible, spawning newer generation of neural electrodes [17–20]. As a result, MEMS-based microelectrodes have, in general, enabled miniaturized and low-power high-density

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http://dx.doi.org/10.1016/j.mee.2014.11.013
0167-9317/

multisite arrays capable of interrogating a wider area. Due to the ease of manufacturing and structural flexibility that they offer, there has also been an increase in interest in polymer-based microelectrodes, particularly for ECoG (electrocorticography) applications [21–26]. Tsang et al. had reported a flexible multisite microelectrode array of several electrodes for insect flight biasing using neural simulation [21]. Rubehn et al. reported independently addressable 252-channel epicortical ECoG electrode array made of platinum electrodes on polyimide foil substrate [22]. A stretchable electrode array for non-invasive wearable applications was developed by Ma et al. who used PDMS (poly dimethylsiloxane) substrate along with metal electrodes. Their array was, however, limited to EMG (electromyography) and EEG (electroencephalography) with no reported application in neural probing at the cortex or brain [23].

As further progress in robust long-term clinical application of bio-probes is pursued, one of the fundamental challenges encountered in recording electrical and electrochemical signals from implantable probes is their long-term high-fidelity performance [27]. As implanted devices, electrodes face a dynamically changing harsh biological environment where pH and ionic concentration fluctuate, and physical arrangement of blood vessels and neurons, for instance, shift [27,28]. On the other hand, from tissue point of view, long-term implantable electrodes pose mechanical and electrochemical strains that affect the structure and health of cells of interest. Therefore, the minimization and elimination of these chronic detrimental interactions between electrodes and tissue is a major research focus. For this, the major barriers that need to be overcome are the mismatch in mechanical stiffness, hardness, electrical impedance, and electrochemical behavior of the electrodes with that of tissue, which cause damages and risks associated with long-term tissue responses to implanted electrodes [28].

To overcome these barriers, therefore, we investigate and report on minimization of these mismatches by using new class of electrode materials that are amenable to material property tailorability as well as lithographic patterning, such as glassy carbon which is derived from the pyrolysis of negative-tone resist polymers. These GC electrodes (henceforth referred to us GC-MEMS) made from lithographically patterned pyrolyzed polymers have excellent conductivity, electrochemical stability in ionic solutions and excellent response to chemical treatments for surface property modifications [29,30]. In addition, GC-MEMS offers ability to tailor its mechanical, electrical, and electrochemical properties by varying pyrolysis conditions such as maximum temperature, duration of pyrolysis, and ramp rate. Utilizing these unique properties of GC-MEMS, we introduce microelectrode structures suitable for μECoG arrays with, (i) tailorable mechanical stiffness that is more compliant than RIE (reactive ion etched) silicon shanks or metals, offering a much better stiffness-matching with tissues, (ii) tailorable hardness for a better hardness-matching with soft tissues, and (iii) tailorable electrical and electrochemical characteristics for better impedance and electrochemistry matching with neurons and tissues. Validation of GC-MEMS electrodes as neural probes is presented through *in vivo* tests.

2. Methods and materials

The platform used in this research for evaluating the tunability of glassy carbon structures consists of microelectrode arrays of (i) tall cylindrical pillars of final dimensions of 700 μm height and 700 μm diameter and (ii) short cylindrical pillars of final dimensions of 20 μm height and 700 μm diameter. The tall pillar sizes correspond to dimensions of penetrating electrodes and offer convenient dimensions for mechanical and electrical characterizations while the shorter pillars correspond to actual sizes of microelectrodes used in μECoG systems. The microfabrication process consists of the traditional negative lithography processes followed by pyrolysis, as shown in Fig. 1 and as reported extensively in our previous works [31–34]. In summary, the process starts with deposition of negative tone SU-8 resist (MicroChem, Boston, MA) followed by lithography for patterning the microelectrode array. Subsequent to lithography, pyrolysis is carried out in a closed ceramic tube-furnace (Lindberg Division of Sola Basic Industries of Watertown, WI) in vacuum or forming gas (95% N_2 and 5% H_2) atmosphere through gradual heating to the desired temperature, followed by cooling to room temperature [31,33,34]. The key pyrolysis parameters that affect the chemical, mechanical, electrical, and electrochemical properties of the final glassy carbon structures are rate of heating, pressure level, amount of nitrogen flow, and type of substrate. Out of these, the following parameters were kept constant: (i) continuous nitrogen flow of at least 2 L/min, (ii) partial vacuum, and (iii) SiO_2 substrate.

The parameters that were varied to tune the mechanical, electrical, and electromechanical properties were, (i) maximum temperature of pyrolysis, and (ii) heating protocol that governed temperature ramping, specifically rate of temperature-ramping to the maximum pyrolysis temperature (T_{max}). In this research, we investigated maximum pyrolysis temperatures of 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C, under ramping time of 2–8 h to T_{max}. The corresponding heating protocols are illustrated in Fig. 2a. For example, for 1000 °C pyrolysis temperature, two protocols are shown. In the first protocol, a total of 5 h were required, with ramping from room temperature to 1000 °C done in 2.0 h (ramping

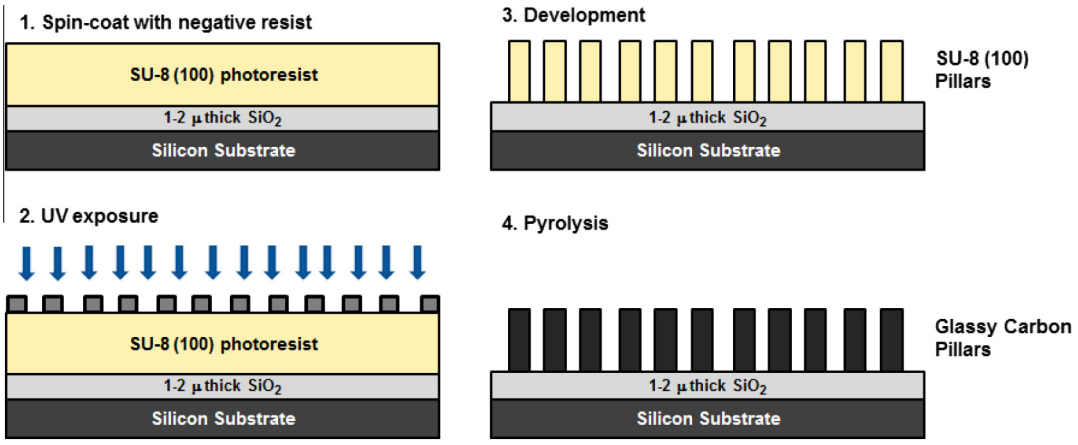

Fig. 1. Lithography and pyrolysis process for fabricating glassy carbon electrodes from a negative tone photoresist. Silicon substrate with oxide layer is used.