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Sputtered iridium oxide modified flexible parylene microelectrodes array for electrical recording and stimulation of muscles

Xiaoyang Kang[a], Jingquan Liu[a,*], Hongchang Tian[a], Bin Yang[a], Yanna NuLi[b], Chunsheng Yang[a]

[a] National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Key Laboratory of Shanghai Education Commission for Intelligent Interaction and Cognitive Engineering, Collaborative Innovation Center of IFSA, Department of Micro/Nano Electronics, Shanghai Jiao Tong University, Shanghai, 200240, China

[b] Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

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ABSTRACT

Here we report the flexible parylene microelectrodes array modified by sputtered iridium oxide film (SIROF) for electrical recording and stimulation of muscles. By using an optimal deposition condition of SIROF that the oxygen flow is 25 sccm and the sputtering pressure is 4.2 Pa, the SIROF modified flexible parylene microelectrodes are successfully fabricated. Combing with the advantages of parylene and SIROF, the microelectrodes show excited mechanical and electrochemical properties, which are capable of electrical recording and stimulation with remarkable performances. Based on experimental results and theoretical calculation, the averaged thermal noise amplitude for SIROF recording sites is $3.83 \pm 1.02\ \mu V$ which is only 10.4% of the Au recording sites as $36.87 \pm 21.39\ \mu V$. These features increased the signal-to-noise ratios (SNR) of the recorded electromyography (EMG). The maximum SNR of SIROF microelectrode and bare gold microelectrode could reach 29.27 dB and 0.47 dB, respectively. Furthermore, the SIROF microelectrode could safely deliver the stimulation current as high as 400 μA which resulted a large charge injection capacity as 3.54 mC/cm^2. The preliminary animal experiments also validated the feasibility of SIROF microelectrodes in electrical stimulation.

1. Introduction

Parylene microelectrodes have been widely used in electrical recording and stimulation applications as the neural interfaces or neural prosthesis [1–6], such as the flexible parylene-based microelectrode arrays for high resolution electromyography (EMG) recordings in a tobacco hornworm [3], the parylene-based three-dimensional microelectrode array for use in retinal prosthesis [5], the flexible parylene-based high-density electrode arrays used for functional electrical stimulation in retinal and spinal cord prosthetics [6], etc. For microelectrodes fabrication, parylene has been extensively used as the structural material based on the advantages of its pinhole-free conformality, low water permeability, chronic implantability as a Class VI material, and its high flexibility and mechanical strength [5–13]. It is important to have the electrodes on flexible substrates like parylene. Compared with the rigid substrates, the flexible substrates could make the electrodes with targeted tissue well contacted, which is more suitable for the complex morphology of muscles and cortex in surface electrical recording and stimulation applications. Because the flexible substrates can reduce the mismatch of mechanical strength between electrodes and tissue, the mechanical damage and immune responses are significantly reduced when the electrodes are implanted inside the muscles and cortex.

Noble metals, such as platinum and gold, are the common materials for neural recording and stimulation microelectrodes due to their resistances to corrosion [5,14]. Of course, these noble metals are available in most MEMS labs. However, the impedance and charge storage capacity (CSC) are two critical parameters for microelectrode performances [15–18]. For the microelectrodes with same size, to effectively fulfill the function of electrical recording and stimulation, the impedance of the microelectrodes should be as small as possible and the CSC should be as large as possible. Unfortunately, the microelectrodes based on platinum and gold are terrible in these electrochemical properties. To reduce the impedance and increase the CSC of microelectrodes,

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* Corresponding author at: Department of Micro/Nano Electronics, Shanghai Jiao Tong University, Dongchuan Road 800, Shanghai 200240, China. Tel.: +86 021 34207209; fax: +86 021 34206883.
E-mail addresses: jqliu@sjtu.edu.cn, xykang@sjtu.edu.cn (J. Liu).

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Table 1
Comparisons of the fabrication process of sputtered iridium oxide film (SIROF) electrode.

Substrate or first layer dielectric	Second layer dielectric	Electrode size	Patterning methods and minimum line width	SIROF methods	References
Oxidized Si substrates	None	0.503 cm^2	None	DC reactive sputtering	[35]
Si substrates	Parylene C	7850 μm^2	Lift-off using photoresist (1000 μm)	Reactive RF sputtering	[36]
Not mentioned (maybe Si-wafer)	None	0.5 cm^2	None	Pulsed dc-sputtering	[37]
Liquid crystal polymers	Liquid crystal polymers	1 mm^2	None	Reactive sputtering	[38]
Oxidized Si-wafer	None	0.5 cm^2	None	Reactive magnetron sputtering	[39]
Silicon nitride	Parylene C	0.64 mm^2	Lift-off using photoresist (800 μm)	Pulsed-DC reactive sputtering	[40]
Polyimide	Polyimide	0.675 mm^2	A LOL 2000 lift-off layer (150 μm)	RF magnetron sputtering	[41]
Polyimide	Polyimide	1960–125,600 μm^2	Lift-off using photoresist (50 μm)	DC reactive sputtering	[42]
Oxidized Si-wafer	None	0.5 cm^2	None	DC magnetron sputtering	[43]
Oxidized Si substrates	None	0.503 cm^2	None	Reactive RF-powered sputtering	[44]
Not mentioned (maybe Si-wafer)	Not mentioned	0.05 cm^2	Lift-off (1262 μm)	Reactive sputtering	[45]
Si-wafer	Parylene C	~2000 μm^2	None	DC reactive sputtering	[46]

many kinds of materials such as Titanium nitride (TiN) [19], Pt black [20], Au black [21], carbon nanotubes [22], graphene and poly(ethylenedioxythiophene) (PEDOT) [23] have been used. Except TiN, the other materials are usually fabricated by electrodeposition process that the adhesion between these materials and microelectrodes are considerably poor. For TiN, the electrical charge is injected through the electrode-electrolyte double layer. Although its charge injection process is safe and ideal for electrical stimulation, the CSC is smaller than the redox materials.

Based on reversible Faradaic reaction of Ir (IV)/Ir (III) surface redox couple, iridium oxide shows large CSC and small impedance. It is considered as a good candidate material for electrical stimulation and recording [2,24]. Iridium oxide film also has performed outstanding stability over wide pH ranges, rapid responses, less potential drift and high durability [25–27]. Thus, the iridium oxide based pH sensor on flexible substrates could also be used for in vivo biomedical, clinical or food monitoring applications. The sensing and actuating functions of the parylene microelectrodes as the electrical recording and stimulation of muscle and neural tissues could be expanded. It is promising for the iridium oxide modified parylene microelectrodes to sense the pH responses of the tissues at the same time.

There are different kinds of iridium oxide, including the thermal iridium oxide film (TIROF) [28], electrodeposited iridium oxide film (EIROF) [29–31], activated iridium oxide film (AIROF) [32–34] and sputtering iridium oxide film (SIROF) [35,36]. For flexible parylene microelectrodes, the TIROF need high temperature in the range of 600–800 °C which is not acceptable for parylene. Although EIROF has very large CSC and small impedance, it is fabricated by the electro-deposition process which has the general problems of the process as discussed above. The AIROF is formed by electrochemical activation of Ir metal to form hydrated iridium oxide film as $IrO_2 \cdot H_2O$ or $IrO(OH)_2$. In practice, the water molecule in AIROF is easy to lose that the electrochemical performance is hard to maintain in a long service time.

The SIROF is formed by reactive sputtering from Ir metal in an oxidizing plasma. It has large CSC and small impedance due to fast and reversible faradaic reaction involving reduction and oxidation of Ir (IV)/Ir (III) surface redox couple. The electrochemical performance could be maintained in a long service time and its stability is also good. What's more, it is compatible with the integrated circuit (IC) and MEMS process [37,38]. Thus, it is reasonable to expect the SIROF modified flexible parylene microelectrodes have good electrochemical properties, which is the basis of electrical recording and stimulation with remarkable performances.

However, there is one problem when the two advantages of parylene and SIROF are combined. That is the integrity of parylene layers during the sputtering process. Table 1 shows the comparisons of the fabrication process of SIROF electrode. Disappointed, most reports focused on the macro electrodes. A few literatures reported the microelectrodes with SIROF, but they were on the rigid substrates. As we know, the glass transition temperature of parylene C is less than 90 °C and the melting temperature is 290 °C [47]. What's more, the tensile strength of parylene C is only 68.9 MPa and yield strength is 55.2 MPa [48,49]. Because the process of the reactively sputtered iridium oxide is an exothermic reaction, the parylene layers are easy to blister or crack from the wafer due to the thermal and mechanical properties of parylene, which results in the failure of fabrication. As a result, the flexible SIROF electrodes reported so far were fabricated from polyimide and liquid crystal polymers as shown in Table 1. The reason is that these materials could tolerate a temperature as high as 350 °C under inert conditions. For parylene C, although these authors did not mention, but the potential reasons that they fabricated the iridium microelectrodes [6,14] rather than the iridium oxide microelectrodes are similar to the problems as discussed above. It should be noted that they even used the new high-temperature stable parylene HT to enable the fabrication of flexible iridium electrode arrays. However, this study focused on the common parylene as parylene C which was more accessible and extensively used.

Based on our previously study [36,50], by depositing the SIROF with appropriate conditions on the pre-annealed parylene layers, the SIROF modified flexible parylene microelectrodes were successfully fabricated. Combining the advantages of parylene as the structural material and SIROF as the good electrochemical modification material, the electrochemical properties of the microelectrodes were measured and shown remarkable performances. What's more, the preliminary animal experiments were also conducted to validate the feasibility of the SIROF microelectrodes for electrical recording and stimulation.

2. Experimental details

2.1. Flexible parylene microelectrodes array fabrication

Fig. 1 shows the fabrication process of the sputtered iridium oxide modified flexible parylene microelectrodes. At first, a 5 μm thick parylene layer was chemical vapor deposited (CVD) on the quartz wafer in a PDS2010 system (Specialty Coating Systems, USA).