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Iridium oxide on indium-tin oxide nanowires: An all metal oxide heterostructured multi-electrode array for neuronal interfacing

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ABSTRACT

All metal oxide heterostructured multielectrode arrays consisting of indium-tin oxide nanowires (ITO NWs) and an iridium oxide (IrO_x) layer were fabricated. The needle-type ITO NWs were grown on an ITO electrode using a radio frequency magnetron sputtering technique followed by electrodeposition of an IrO_x layer. The major advantage of this fabrication technique is in its simplicity because it does not require templates and seed layers to grow the ITO NWs. A transmission electron microscope found the IrO_x to be uniformly electrodeposited over the surface of the ITO NW. After the electrodeposition process, the charge storage capacitance (CSC) of the ITO NW electrode increased from 0.09 to 4.25 mC cm^{-2}, and the IrO_x/ITO NW electrode exhibited a charge injection limit of 1.9 mC cm^{-2} and CSC utilization efficiency of approximately 45%. The stimulation performance of the IrO_x/ITO NW electrode was confirmed using rat hippocampal slices, which exhibited a higher negative peak amplitude in the field excitatory postsynaptic potential when stimulated by a single pulse, and more effectively induced long-term potentiation via a theta burst stimulation compared with an ITO NW electrode. These results indicate that the synergetic combination of ITO NWs and a very thin IrO_x layer enhanced the performance of the stimulus.

1. Introduction

Extracellular stimulation of the neural system and the recording of neuronal activities constitute the core processes in many *in vitro* and *in vivo* neural interfacing applications. These applications range from basic studies, such as understanding the electrophysiological mechanisms underlying the learning and memory processes to bi-directional neural interface applications, such as closed-loop brain-machine interfaces, neuromodulation, and prostheses [1–3]. Methods for efficient charge injection without causing damage to neural tissues, and the recording of neural activities with a moderate signal to noise ratio, have been investigated to facilitate stimulation-induced changes in neural activity, such as long-term potentiation or depression. Thus, much effort has been expended to develop electrodes that possess large internal or outer surface areas per projection area, because a large surface area can both reduce the interface impedance and increase the charge storage capacity, which contribute to reducing the noise and increasing the charge injection performance, respectively [4]. Efforts to modify planar metallic electrodes, including those made of gold (Au) or platinum (Pt), with nanostructures, such as nanowires (NWs), nanorods (NRs), nanopores, and nanopillars, have been successful [5,6].

At present, it has become routine to record neural signals with a signal to noise ratio greater than 10 due to the wide range of nanomaterials and fabrication techniques available. However, in view of the stimulation efficacy, the list of electrode materials exhibiting charge injection limits higher than the neural damage threshold of 1 mC cm^{-2} are rather limited. These include iridium oxide (IrO_x) [7], roughened Pt [8], and carbon nanotubes [9]. Of these, IrO_x is the most widely studied electrode material for neural stimulation due to its biocompatibility, high charge storage capacitance (CSC), and high charge injection limit [10]. Even though sputtered IrO_x films (SIROFs) and electrodeposited IrO_x films (EIROFs) exhibit charge injection limits of 1–10 mC cm^{-2}, they require the formation of thick films that have rough surfaces to realize an enhanced CSC [11–14]. Very recently, we electrodeposited a very thin (20-nm-thick) IrO_x layer on the surface of a nanoporous Au (NPG) electrode, which then exhibited a CSC of 8.8 mC cm^{-2} and a charge injection limit of 2.3 mC cm^{-2} [15]. The IrO_x/NPG electrode exhibited a charge injection efficiency, which is defined as the ratio of the charge injection limit to the CSC, of about 25%, which is almost two times higher than that of SIROFs and EIROFs. The enhanced charge injection efficiency has been attributed to the synergetic combination of the NPG with a low pore resistance and a very thin IrO_x with a high

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charge injection capability. Yoon et al. [16] and Yamagiwa et al. [17] electrodeposited IrO_x on electrochemically grown Au NWs using a template and on Pt-black, respectively. Although the CSC of the IrO_x/Au NW and IrO_x/Pt-black electrodes were significantly enhanced compared with that of the Au NW and Pt-black electrodes, no quantitative charge injection limit data were reported.

Since the first report by Gross et al. [18] on the use of optically transparent and electrically conductive ITO in multielectrode array (MEA) fabrication, ITO-coated glass has been widely used in MEA fabrication as a substrate when forming transparent base electrodes, leads, and pads [19,20]. Even though some ITO electrodes have been used as stimulation electrodes when observing electrically evoked calcium transients of the retina [21–23], cultured neurons [24], and stem cells [25], they are not used as the principal electrodes for MEAs due to the high electrochemical impedance of planar ITO electrodes. In this study, to enhance the neuronal signal recording and electrical stimulation performance of ITO electrodes, we modified an ITO electrode with ITO NWs. For this, we employed RF magnetron sputtering of an ITO target to form ITO NWs on the ITO electrode. In addition we electrodeposited IrO_x on the ITO NWs to utilize the synergetic effect of the large surface area of ITO NWs and efficient charge injection capability of the IrO_x layer. In this report, we present the details of the fabrication of the ITO NW and IrO_x/ITO NW electrodes together with their electrochemical properties, which include the charge injection limit and the *in vitro* neuronal recording and stimulation performance when applied to rat hippocampal slices. We also report on the ITO NW structure tuning capability of RF magnetron sputtering.

2. Experimental

The ITO MEA was fabricated and used as a starting electrode array to grow ITO NWs. The fabrication process for the ITO MEA and IrO_x/ITO NW-modified ITO MEA is schematically represented in Fig. 1.

2.1. Fabrication of ITO MEA

First, 300 ± 1.8 nm thick ITO-coated non-alkaline glass (Eagle 2000 EXG, sheet resistance of 4.5 ± 0.27 Ω/□) with dimensions of 50 mm × 50 mm × 0.7 mm was cleaned with a cleaning solution. Then, the ITO layer was patterned using standard photolithography and ITO wet etching techniques to have an 8 × 8 electrode layout, leads, and pads that were sized to fit a commercial MEA 1060 amplifier (Multi Channel Systems). The diameter of an active ITO electrode and the center-to-center distance between two adjacent electrodes were 25 μm and 200 μm, respectively. A bi-layer lift-off resist technique and RF sputter deposition of SiO_2 were employed for passivation of the ITO electrode [26,27]. Briefly, an overhang structure was constructed by applying conventional photolithography and using both UV-insensitive lift-off resist and UV-sensitive negative resist. Then, RF sputter deposition of SiO_2 was applied followed by lift-off of the overhang structure to produce the ITO MEA. The detailed fabrication conditions and material information for each unit process depicted in Fig. 1 are listed in Table S1.

2.2. Growing the ITO NW and fabricating the ITO NW MEA

RF magnetron sputtering under oxygen deficient conditions was employed to form the ITO NW. All samples were placed face-down on a substrate heater and 3-mm-diameter indium (In) metals were placed on the 4-inch ITO target (purity 99.99%, In_2O_3 : SnO_2 = 90 : 10 (w/w), KOJUNDO CHEMICAL) along the circular erosion band. Prior to formation of the ITO NW on the ITO MEA, preliminary growth was performed using the same ITO-coated non-alkaline glass to observe the effect of the sputtering conditions, such as the RF power (200–300 W), working pressure (2.5–20 mTorr), substrate temperature (250–550 °C), substrate-to-target distance (6–8 cm), and the number of In metals (0–32), on the growth of the ITO NWs. The surface morphology and cross-sectional structure of the ITO NWs was investigated using a field emission scanning electron microscope (FESEM, FEI-SIRION 400) and a

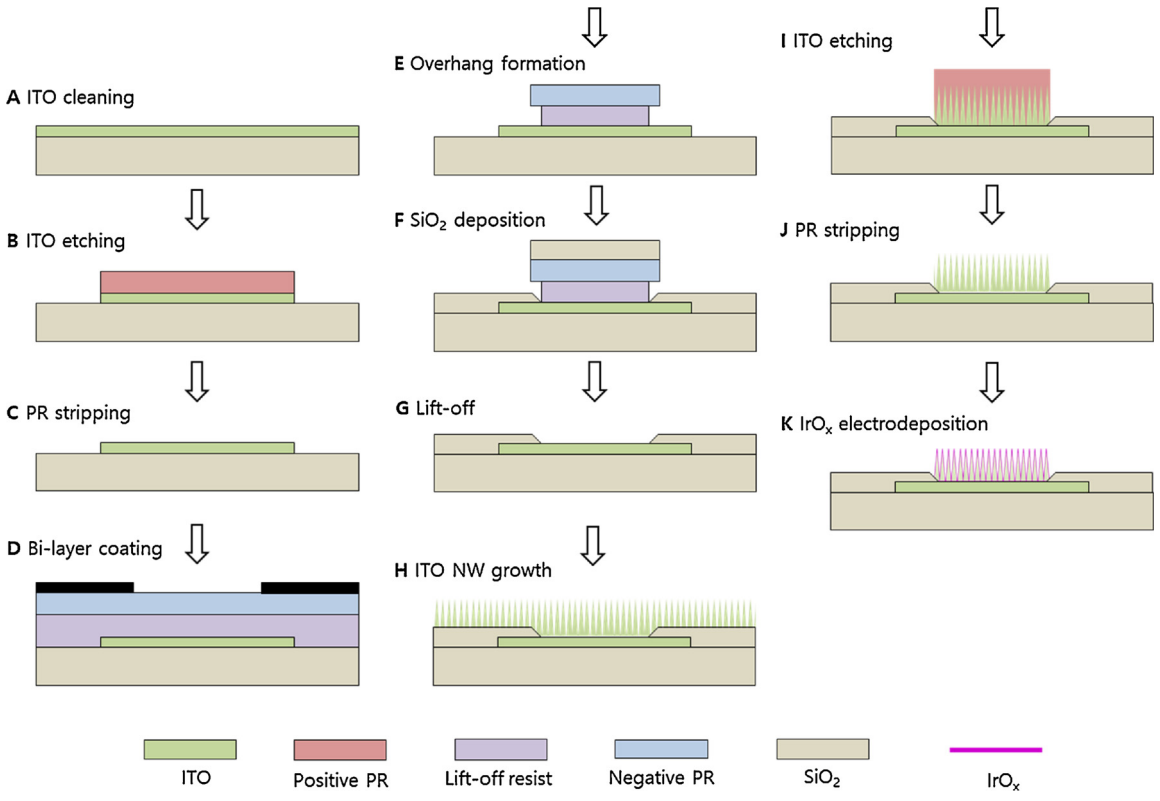

Fig. 1. Schematic representation of the ITO MEA and IrO_x/ITO NW-modified ITO MEA fabrication process.