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Highly Efficient Cold Sputtered Iridium Oxide Films for Polyimide based Neural Stimulation Electrodes

Shin Ae Kim[1,2], Eui Tae Kim[1,2], Sung June Kim[1,2]

[1]*School of Electrical Engineering and Computer Science, Seoul National University, Kwanak-Gu, Seoul, Republic of Korea*
[2]*Nano Artificial Vision Research Center, Seoul, Republic of Korea*

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Abstract

Iridium oxide films (IROFs) have been extensively studied as a material for electrical stimulation of neurons, as iridium oxide has higher charge storage capacity than other metal films. More recently, sputtered iridium oxide film (SIROF) has been studied, because it can be made more conveniently than activated iridium oxide film (AIROF). Typically, the SIROFs are grown at temperatures from 400 to 600 ℃. However, such high temperatures cannot be used when the iridium oxide (IrOx) film is to be deposited on a flexible polymer material, such as polyimide. In this paper, we show that we can still obtain excellent characteristics in SIROFs grown without heating (cold SIROF), by optimizing the growth conditions. We show that the oxygen flow rate is a critical parameter for controlling the surface properties of a cold SIROF. At an oxygen flow rate of 12 sccm, the cold SIROF exhibited a charge storage capacity (CSC) of 60 mC/cm^2, which is comparable to or better than other published values for iridium oxide films including heated SIROFs. The film produced under these conditions also had the minimum impedance value of all cold SIROFs deposited for this study. A stability test and biocompatibility test also demonstrated the superiority of the optimized cold SIROF.

Key words : SIROF, Cold sputtering, Polyimide microelectrode, Implantable material, Neural prostheses

Ⅰ. INTRODUCTION

People with profound hearing or vision impairments can now hear or see through direct electrical stimulation of neurons, using neural prosthetic devices [1-10]. Safe and effective electrical stimulation can be obtained using electrode arrays made of metals such as platinum, gold, iridium oxide, titanium nitride, and platinum-iridium [11-23]. Among these, iridium oxide has drawn significant attention, due to its high charge storage capacity (CSC) [11-20, 23]. With high CSC, electrical charge can be delivered to neural tissues in high density, thus creating effective electrical stimulation. Conventionally, an iridium oxide film can be obtained by first depositing an iridium film on a substrate by sputtering or e-beam evaporation, and then by oxidizing it in ambient oxygen outside of the deposition chamber. This is called an activated iridium oxide film (AIROF). Alternatively, an iridium oxide film can be obtained by sputtering iridium in ambient oxygen. The latter method is favored, because it is more convenient and excellent film characteristics have been obtained. The deposition of sputtered IrOx film (SIROF) is performed with the substrate heated to elevated temperatures, which can range from 400 to 600 ℃ [14,16,18,20]. However, in neural prosthetic applications, such as retinal prosthesis, a flexible substrate may be required, so a polymer material, such as polyimide, may be used [1,5,10]. A polyimide substrate cannot be heated above its curing temperature of 300 ℃; therefore, sputter deposition at an elevated temperature is prohibited. Thus, we have tried to produce SIROFs without substrate heating (cold SIROFs), and in this paper, we show that by optimizing the growth conditions we can still obtain excellent characteristics in cold SIROFs.

Corresponding Author : Sung June Kim
Room 1006, Bldg #301, Seoul National University, San 56-1, Sillim-dong, Kwanak-gu, Seoul, Republic of Korea, 151-742
Tel : +82-2-880-1812 / Fax : +82-2- 882-4158
E-mail : kimsj@snu.ac.kr

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Ⅱ. MATERIALS AND METHODS

A. Preparation of IrOx electrodes

A schematic diagram of the fabrication process is presented in figure 1. A silicon substrate with a 2 μm thick silicon oxide layer on top was used as a starting material. A polyimide (PI2525, HD Micro Systems) was spin coated at 3500 rpm to a

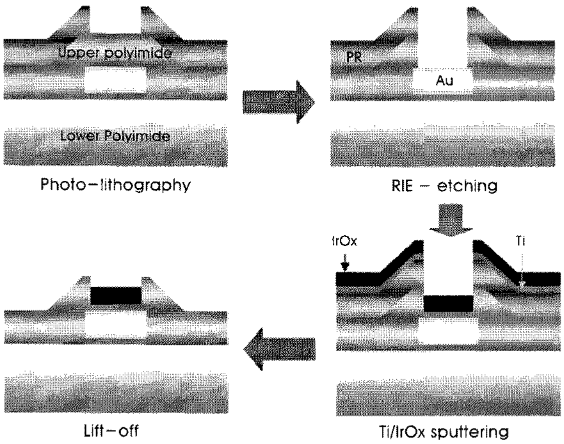


Fig. 1. Schematic of iridium oxide process technology based on polyimide, for retinal electrodes.

thickness of 6 µm. Before the polyimide coating, an adhesion promoter (VM652) was spin coated. The polyimide film was cured on a hot plate at 300 ℃. After 24 hr of stabilizing time, Ti/Au was deposited by sputtering and patterned by photolithography, to form the interconnection lines. Then, a 6 µm thick upper polyimide layer was coated, with the same process as the lower polyimide layer. The latter forms the insulating layer for the interconnection lines. After opening the upper insulation layer for the electrode sites and contact pads, Ti / IrOx was deposited by sputtering (Korea Vacuum Co.), using Ti and Ir targets sequentially. Sputtering was done with Ar in ambient oxygen. The substrate was unheated during the sputtering process. The Ar flow rate was fixed at 40 sccm (standard cubic centimeter per minute), and the oxygen flow rate was varied from 4 to 40 sccm. The thicknesses of the Ti and SIROF were 200 nm and 800 nm, respectively. The IrOx layer was patterned by lift-off, using previously defined photoresist patterns. The area of the fabricated IrOx electrode sites was 432,000 μm^2. Table 1 lists the deposition parameters used in this study.

B. Measurements

A potentiostat (IM6e model, Zhaner Inc.) with a three electrode cell configuration, consisting of an Ag | AgCl reference-electrode, a large-area Pt counter-electrode, and the IrOx electrode under test, was used to test the charge storage capacities (CSC) of the films. A cyclic voltammogram (CV) was taken, and the CSC was calculated from the CV. A phosphate-buffered saline (PBS) solution with a pH of 7.4 was used. All CVs were measured with a 50 mV/s sweep rate, between potential limits of -0.8 V and 0.6 V. Then, the CSC was calculated from the time integral of the current.

The thicknesses of the films deposited on the substrate were determined by a KLA-Tencor Alpha step profiler, and the surface morphologies and roughnesses of the SIROFs deposited at various oxygen flow rates were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM; XE-150, PSIA) in contact mode, with a constant scan

Table 1. IrOx deposition conditions.

Target	Iridium, pure metal
Substrate	Ti (adhesion layer) / Polyimide / SiO_2 / Si
Substrate temperature	Below 100℃
Deposition time	30min
Working gas flow ratio	Argon 40 sccm, Oxygen 4 ~ 40 sccm
Working pressure	20 mtorr
Input power	200 W DC power

rate of 1 Hz. The influence of the long-term test was analyzed by CV curves and SEM images.

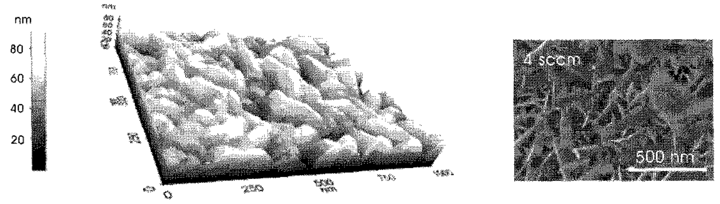
The bonding of the deposited SIROF to the substrate was also tested. Tape (3M, Scotch Magic Tape 810) was applied to a test area of the SIROF. Adhesion was considered adequate if the SIROF surface was not pulled off with the tape when it was removed. Impedance measurements were performed before and after this test, for comparison.

C. Biocompatibility test (cell culture and immunostaining)

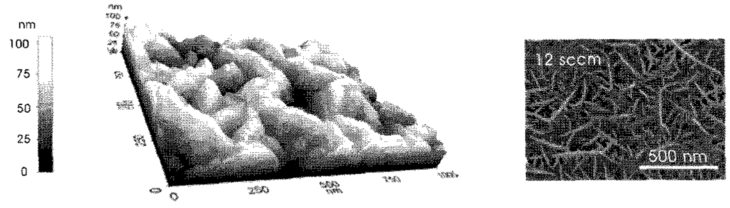
Hippocampal neurons were obtained from embryonic rats, and dissociated into single cells by trypsin treatment and mechanical trituration. The dissociated cells were placed on a poly-L-lysine (PLL) coated substrate, at a low density of 78 cells/mm^2, in a Neurobasal medium (GIBCO) supplemented with B27 and L-glutamine. The cells were allowed to attach to the surface for 7 hours, after which the unattached materials were removed from the surface by exchanging the culture medium. The cultures were then maintained at 37 ℃, under 5% CO_2. The attachment and outgrowth of living neurons were observed using both SEM and an inverted microscope equipped with phase contrast optics. In addition, 4'-6-Diamidino-2-phenylindole (DAPI) staining was utilized to determine the number of live cells, for clear discrimination.

Ⅲ. RESULTS AND DISCUSSION

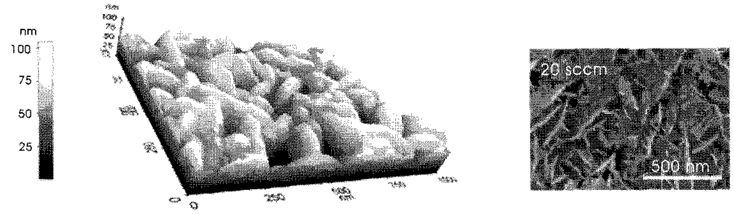
A series of depositions was performed, in order to investigate the dependence of the CSC of the SIROFs on the growth conditions. The effect of oxygen on the SIROF was studied by varying the oxygen flow rate from 4 to 40 sccm. Figure 2 shows that the SIROFs fabricated at different oxygen flow rates had different roughness factors. The film roughness was maximized at 12 sccm of oxygen. The deposition rates and the roughness factors of the SIROFs deposited at different oxygen flow rates were measured, and are summarized in table 2. The average (R_a) and peak- to-valley (R_{pv}) roughness factors, as well as the deposition rates, increased with increasing oxygen flow rate until they peaked at 12 sccm, and then decreased with further increases in the flow rate.



(a) O_2 = 4 sccm



(b) O_2 = 12 sccm



(c) O_2 = 20 sccm

Fig. 2. AFM and SEM images of cold sputtered iridium oxide surfaces obtained at three different oxygen flow rates. The surface roughness increased with increasing oxygen flow rate up to a maximum at 12 sccm, and decreased at higher oxygen flow rates.

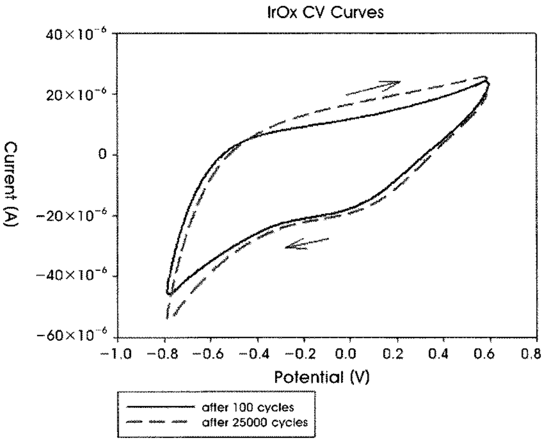


Fig. 3. CV-curves of unheated SIROF after a short number of cycles and after a long-term test. IrOx electrodes have been proven to withstand more than 25,000 cycles at 100 μA current amplitude, without degradation.

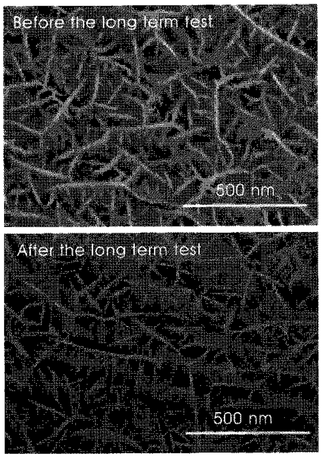


Fig. 4. SEM images of SIROF surface. No regeneration or collapse of structures was observed after the long-term cyclic CV runs.

Cyclic voltammetry (CV) curves of selected SIROF samples were also tested, by using a potentiostat in PBS. The voltage was linearly scanned from -0.8 V to 0.6 V, at a scan rate of 50 mV/s. Typical CV curves are shown in figure 3. Charge storage capacity values were calculated from the CV curves as explained in the Methods section. The CSC values of the SIROF films changed as the oxygen flow rate varied from 4 to 40 sccm, and are also summarized in table 2. The maximum CSC value, 60 mC/cm^2, was obtained at an oxygen flow rate of 12 sccm.

Long term safety and stability are required for implantable stimulating electrodes. For our films, the maximum CSC value obtained at initial activation increased slightly, from 60 to 64 mC/cm^2, with no failure after 25,000 potential cycles over a 2 week test period, as shown in figure 3. The morphology of the film was compared before and after the 25,000 cycle run. As shown in the SEM image of figure 4, subsequent potential cycling within the voltage range - 0.8 V to 0.6 V did not seem to change the film's morphology. The lack of significant changes in the CV data and the SEM image shows that mechanical stress does not change the electrochemical characteristics of the unheated SIROF.

Another stability test was performed using scotch tape. The tape was placed on the surface of the substrate at the electrode sites, and then removed as quickly as possible by hand. Failure could occur at the weakest point of the system, mostly likely at the junction of the SIROF-polyimide films. In our tape test, however, the SIROF-polyimide interface was never exposed, and the impedance of the film stayed at its initial value. Figure 5 shows the values of the impedance before and after the tape test.

The biocompatibility of the stimulating electrode is also important. Cultured Hippocampal neurons, from 18 day-old embryos, were grown on the SIROF electrode coated with PLL. After a 3 week test period, the neurons exhibited good affinity to both the polyimide and the SIROF surfaces.

Table 2. Deposition rates, roughness factors, and charge storage capacities of unheated IrOx deposited at different oxygen flow rates.

O_2 (sccm)	4	8	12	16	20	40
Deposition rate (nm/hr)	27.9	130.0	1085.5	1070.5	470.0	320.2
R_{pv} (nm)[a]	91.243	90.952	104.610	98.943	98.481	88.414
R_a (nm)[b]	10.796	11.170	15.492	12.968	13.048	7.504
CSC (mC/cm^2)	37	44	60	58	54	53

[a] Rpv : peak-to-valley roughness
[b] Ra : average roughness

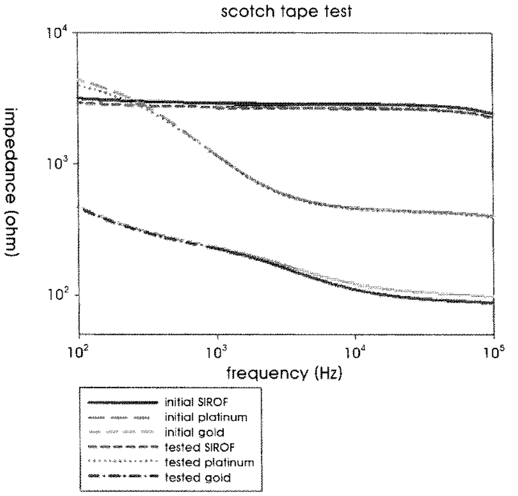


Fig. 5. The resistivity values of the SIROF before and after tape testing, compared with those of gold and platinum. It can be seen that the cold sputtered SIROF is stable, and the resistance values are stable, as in platinum and gold.

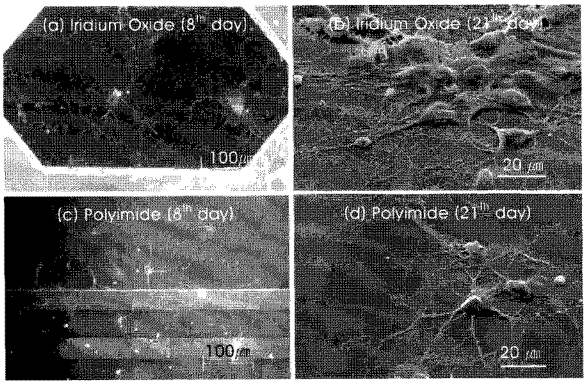


Fig. 6. Confocal and SEM images of Hippocampal neurons cultured on (a, b) the SIROF surface (dark area) and (c, d) the polyimide layer. The neurons showed good affinity to both the SIROF and the polyimide, which is a well-known biocompatible material.

AxioCam HR (Karl Zeiss, Germany) and SEM images of the hippocampal neurons are shown in figure 6, taken after 8 or 21 days from the primary culture. For more minute images of neuronal affinity and connections, the samples were dried on the 21st day, using a critical point dryer (BAL-TEC, USA), and then coated with gold before the SEM observation. As shown in figure 6, the neurons exhibited a number of well-connected dendrites, whether they were on the cold sputtered iridium oxide surface (figure 6 a,b) or on the polyimide surface (figure 6 c,d). There was no noticeable difference in the measured cell densities on either surface. Using DAPI staining, we estimated that there were ninety live nuclei on the SIROF, and there was also no obvious difference between the 8th and 21st day.

A good stimulating electrode is characterized by a large active surface area. The actual surface between the electrode and electrolyte is determined by the roughness of the electrode surface. When the roughness and porosity factors of the morphology increase, the actual surface for an active chemical reaction is increased. At higher oxygen concentrations, it is possible to achieve higher oxygen surface coverage of the iridium. However, when the oxygen coverage is above its optimal value, the site material may actually have fewer reactions with oxygen [13, 16].

At optimal oxygen flow, the maximal consumption of oxygen occurred at the active surface, which could be confirmed by the deposition rates and roughness factors of the electrode surface. In our investigation, the surface roughness increased with increasing oxygen flow rate, reached a peak at 12 sccm, and then decreased at higher oxygen flow rates. The deposition rate was also dependent on the oxygen flow rate, and also reached its maximum at an oxygen flow rate of 12 sccm.

Our best cold SIROF CSC value of 60 mC/cm^2 was similar to reported values for an AIROF (around 60 mC/cm^2; C.-S. Kim et al. 2004) that was activated with - 0.85 / + 0.75 V for 800 cycles. Our best value was also higher than the previously reported values obtained from a heated SIROF (32 mC/cm^2; J. D. Kleins et al., 1989) and from an unheated SIROF (18.9 mC/cm^2; Sachin S. Thanawala et al., 2008). It was also considerably higher than the published values obtained with TiN (22 mC/cm^2; James D. Weiland et al., 2002), PtIr (5.6 mC/cm^2; Stuart F. Cogan et al., 2005), Au (5.7 mC/cm^2; E. Slavcheva et al., 2004), and AIROFs (23 mC/cm^2; Stuart F. Cogan et al., 2005).

Ⅳ. CONCLUSION

Safe delivery of a large number of charges to the target cell is important for electrode materials used in neural prosthesis. From this point of view, iridium oxide is a better material than other metal films for microelectrodes used for neural stimulation. We studied the process conditions under which cold SIROFs exhibit the best performance for neural stimulation.

Cold sputtering is necessary for deposition of the films on flexible polymer substrates. Specifically, the decisive role of the oxygen flow rate in determining the surface morphology, roughness, and electrical characteristics of the SIROF has been studied. Cold SIROF embedded polyimide electrodes showed good electrical efficiency, biocompatibility, and stability when subjected to various tests. The charge storage capacity recorded from the fabricated cold SIROFs was similar to, or higher than, other published values for iridium oxide films, including heated SIROFs.

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