Sputtered platinum–iridium layers as electrode material for functional electrostimulation

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ABSTRACT

In this study co-sputtered layers of platinum–iridium (PtIr) are investigated as stimulation electrode material. The effects of different sputter parameters on the morphology and the electrochemical behavior are examined. It is shown that films sputtered at the lowest incident energy possess the highest charge storage capacity (CSC). At a Pt:Ir atomic-ratio of 55:45 the obtained CSC of 22 mC/cm^2 is enhanced compared to the standard stimulation material platinum (16 mC/cm^2) but inferior to iridium which has a CSC of 35 mC/cm^2. Long term cyclic voltammetry measurements show that PtIr can be activated which increases the CSC to 29 mC/cm^2. Also a change in the film morphology is observed. Sputtered platinum–iridium films promise to combine high mechanical strength and increased charge storage capacity.

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1. Introduction

Today an increasing number of medical devices such as pace makers and cochlear implants are dedicated to the functional stimulation of neural cells [1]. Also neural probes and eye implants are being developed [2–5]. One of the largest challenges is the electrode–electrolyte interface between the neuron and the stimulation electrode. The electrical energy has to be transformed to an ionic current which results in a depolarization of the nerve cell evoking an action potential [6]. For example, in Ref. [3] the retinal ganglion cells are stimulated with 25 iridium oxide electrodes. For a further increase of the optical resolution a reduction of the electrode size is essential. At the same time the necessary charge to evoke an action potential has to remain constant. Furthermore, the voltage range has to be kept in a safe range to prevent any irreversible electrode alteration and electrolysis of the interstitial fluid. Viable solutions are to optimize the electrode geometry [7] or the stimulation electrode material.

Typical electrode materials are platinum, platinum–iridium [8,9], titanium-nitride [10], iridium [11], and iridium oxide [12–17]. These materials can be differentiated into three groups: a) titanium-nitride which has a pure capacitive charge transfer from the electrode into the electrolyte; b) platinum, iridium, and platinum–iridium where reversible Faradaic reactions take place at the electrode surface in addition to the capacitive charge and c) iridium oxide which transforms into a hydrated oxide film with a high charge injection capacity [18].

Platinum–iridium is used as a stimulation electrode material because of its increased hardness, corrosion stability and enhanced charge injection capacity compared to pure platinum [19]. The material is commercially available as alloyed wire-stimulation electrode (FHC Inc., Bowdoin, ME, U.S.A., or Heraeus AG, Germany).

Platinum–iridium thin films can be applied to microelectronic devices by electroplating [20], chemical reaction [21,22], or sputtering techniques [23]. The latter method allows the deposition of elements and compounds with adapted performance. Through variation of the sputtering parameters like power, pressure, distance between target and substrate (working distance, WD), and gas flow the composition, roughness, stability, and charge storage capacity (CSC) can be customized. The parameter CSC, Q_{CSC} also called Cathodic Storage Capacity is a measure for the highest possible charge that an electrode material can accumulate and transfer safely through the electrode/electrolyte phase boundary [18]. It is commonly used for electrochemical characterization and initial screening of various electrode materials and calculated applying the method of cyclic voltammetry according to Eq. (1):

$$Q_{CSC} = \frac{1}{v} \int_{E_c}^{E_a} |i| dE \dots \left[mC/cm^2 \right]. \tag{1}$$

with E being the electrode potential vs. Ag/AgCl, i is the measured current density, E_a and E_c are the anodic and cathodic potential limits, respectively, and v is the corresponding potential scan rate. Although, the CSC will not give the possible charge delivered by biphasic pulsing

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(Q_{inj}), which is used for actual stimulations, it is known that typically 5–20% of the Q_{CSC} can be safely transferred into the cells [18].

The parameter pressure, WD and sputtering power can be combined into the parameter mean incident energy (E_{inc}). The kinetic energy of a sputtered particle directly at the target results from the acceleration voltage of the sputtering argon atom, hence from the generator power. The WD and pressure define the amount of collisions that reduce the kinetic energy of the atom on its path to the substrate. The incident energy of an adatom that reaches the substrate is the most important factor for the film growth [11].

In a previous paper it has been shown that thin films of sputtered IrO_x possess excellent properties as stimulating electrode material and superior characteristics such as high CSC (up to 90–95 mC/cm^2), broad safe potential range (−1.1 V to 1.2 V vs. Ag/AgCl) and low impedance in the frequency range below 10 Hz, which is relevant for neural stimulation [24].

So far, no applications of co-sputtered PtIr thin films as stimulation material are known. At the same time PtIr alloys are known for their greater mechanical strength and chemical inertness compared to pure Pt, Ir or IrO_x—a requirement for safe service, especially in long term implantable applications [19].

This paper presents the initial screening of the PtIr sputter process, regarding the applicability of the deposited platinum–iridium thin films as electrode material for neural electrostimulation. Different sets of sputtering parameters are compared and characterized in respect to their influence on the film morphology and electrochemical performance in model physiological solution. To assess the applicability of sputtered PtIr it is compared to sputtered pure platinum and iridium films. Finally, the long term stability and activation of the PtIr films are investigated.

2. Machines and methods

Thin platinum–iridium films were prepared using a Nordiko 2550 magnetron sputtering machine equipped with a titanium (for adhesion layers), a platinum, and an iridium target. The sputtering chamber was evacuated to a base pressure of 0.4 mPa using rotary vane and cryogenic pumps and then fed with argon gas at a constant flow rate of 100 sccm. The pressure was measured with a MKS Baratron pressure gauge and controlled by a throttle, which reduced the pumping speed of the cryogenic pump. The working distance was held at a constant 78 mm. The power generators (a MKS MDX 10 and an ENI RPG 100) can be separately adjusted for co-sputtering. The substrate rotates beneath the targets (Fig. 1) with a constant speed of 8 rev per minute. Measurements of the deposition zones showed smooth deposition profiles that do not overlap. The sputtering parameters are given in Table 1. All films were deposited at room temperature and no significant heating was observed during the processes.
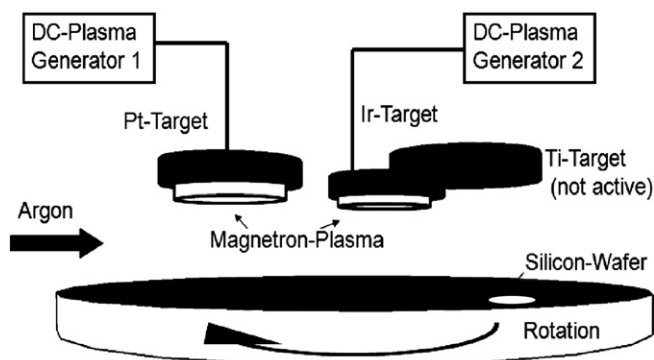

Fig. 1. Scheme of the co-sputtering setup.

Table 1
Sputtering parameters of the films used in this study. The incident energy E_{inc} was derived by the method shown in Ref. [11]. Working distance is the gap between target and substrate. The depositions rate was calculated by division of film thickness through sputtering time. The ratio was calculated by the division of the sputtering rates.

E_{inc} [eV]	10.2	1.9	0.2
Pressure [Pa]	2	9	15
Power [W]	180	1000	180
Working distance [mm]	78	78	78
Deposition rate Pt [nm/min]	10.5	60	7
Deposition rate Ir [nm/min]	7.5	45	5.4
Deposition ratio Pt/Ir	1.4	1.3	1.3
EDX weight Pt|Ir [%]	54.8|45.2	54|46	55.9|44.1
EDX atomic Pt|Ir [%]	54.4|45.6	53.6|46.4	55.6|44.4
EDX atomic ratio Pt/Ir	1.19	1.15	1.25

The deposition rate of platinum is slightly higher than that of the iridium at equal sputtering power. For comparability of the deposited layers the sputtering power ratio was held constant at a fixed ratio of 1:1; resulting in a Pt:Ir atomic-ratio of approximately 55:45 for all PtIr samples, which was verified by energy-dispersive X-ray spectroscopy (EDX) analysis (Table 1). This is in agreement with the deposition rate of the single elements and the slight deviation can be explained by uncertainties of the deposition rates that depend on the statistical process of particle transport through the background sputtering gas. The increased deposition rate of platinum compared to iridium at the same sputtering power is probably due to its lower binding energy and density.

The film thickness was determined using a Tencor P-10 surface profiler and the sputtering time was adjusted to deposit all films with an equal thickness of 200 nm. Previous to the electrode layer a 25 nm Ti adhesive layer was sputtered. Scanning electron microscopy (SEM) images were taken with a Zeiss Gemini 982 electron microscope at 3 kV acceleration voltage and magnifications up to 200.000 with an EDX function (20 kV acceleration voltage at a working distance of 10 cm). An EG&G electrochemical test cell with a circular 0.503 cm^2 opening was used to characterize the unstructured and untreated films on 10 mm (4″) [100] p-silicon wafers from Si-Mat or Carl-Roth super-frost soda-lime glass microscope slides (72 mm × 26 mm). There were no morphological or electrochemical differences noted between films sputtered on different substrates.

The CSC of the working electrodes was determined applying cyclic voltammetry with a scan rate of 100 mV/s in argon purged model physiological saline solution (unbuffered 0.9% NaCl), using an EG&G 283 potentiostat/galvanostat. The cyclic voltammetry (CV) sweeps were taken between −0.9 V and 1.1 V against a Ag/AgCl reference (corresponding to 197 mV vs. the reversible hydrogen electrode RHE) and a Pt counter electrode. These values were chosen since this is the broadest range, where none of the layers tested showed electrolysis effects. All CV curves shown (if not indicated otherwise) are the 5th sweep to give a stabilized curve. The CSC is the integration of the cathodic part of the resulting curve.

3. Results and discussion

3.1. Sputtering parameters

A series of thin PtIr films was sputtered and evaluated varying the already mentioned governing parameters of the sputter process, namely the power and pressure. In this paper we present and compare the composition, morphology, and electrochemical responses of the three most characteristic samples sputtered at different sets of parameters, given in Table 1. Using Monte Carlo method simulations based on findings for iridium [25], we have simulated the transport of the sputtered metal particles and statistically estimated their mean incident energy E_{inc}. Further on in the text, the test samples are referred to by their incident energy.