Nicolai Simon*, Maria Asplund, Thomas Stieglitz and Volker Bucher

Plasma Enhanced Atomic Layer Deposition of Iridium Oxide for Application in Miniaturized Neural Implants

Abstract: High quality recording of neuronal activities and electrical stimulation require neurotechnical implants with appropriate electrode material. Iridium oxide (IrO_x) is an excellent choice of material due to its biocompatibility, low electrochemical impedance, superior charge injection capacity, corrosion resistance, longevity, and electrochemical stability. Plasma enhanced atomic layer deposition (PE-ALD) and a suitable precursor, like (Methylcyclopentadienyl) (1,5-cyclooctadiene) iridium, could be a promising technique to produce highly conformal and performant IrO_x-films at low temperatures and low costs. Various studies have reported the deposition of iridium oxide, but usually at very high temperatures. These processes are not suitable for polymer substrates and limit the use of such post-processing together with active implants. In this work the (Methylcyclopentadienyl) (1,5-cyclooctadiene) iridium(I) ((MeCp)Ir(COD)) precursor was used as a promising approach for depositing IrO_x-films using low temperature PE-ALD. This precursor is normally used for chemical vapour deposition processes. First experiments were carried out on silicon substrates at deposition temperatures of 110 C°. The precursor was heated up to 75 °C and oxygen plasma was used as co-reactant. The deposited films were analysed with EDX and AFM, showing a smooth surface and a promising ratio between the elements iridium and oxygen.

Keywords: PE-ALD, iridium oxide; thin film coating, implants

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1 Introduction

Iridium oxide can be used in many applications due to its catalytic, mechanical, and electrical properties. It is a potential material in the application for random access memories [1], it can be used in organic light emitting diodes (OLEDs) as an interlayer to improve the optical as well as the electrical properties [2] and can also be used as a sensor material for e.g. pH electrodes [3]. In addition to these outstanding properties, iridium oxide also exhibits excellent biocompatibility and high corrosion resistance. Thus, the compatibility between the material and neuronal cells is excellent [4]. Therefore, iridium oxide is a promising electrode material that may improve the performance of neurotechnical implants [5, 6].

Physical vapour deposition (PVD) like magnetron sputtering can be used to deposit the desired films [7], but PVD lags in conformity. Another possibility is to deposit the coating via CVD or ALD. Using ALD processes highly conformal layers can be deposited.

ALD is a cyclic deposition technique to achieve ultrathin films with nearly no defects. In a first step, the substrate is exposed to a precursor, which adsorbs on the surface and reacts in a self-limiting manner. In the second step, the reaction products and unused precursor from the first step are purged out of the reaction chamber with an inert gas, like nitrogen or argon. In a third step the co-reactant, often an oxidant, reactivates the surface of the substrates, whereas in a fourth step another purging step takes place. After that, the cycles are repeated. The film growth proceeds in a layer-by-layer growth, where ideally one molecular layer is deposited at one cycle.

In thermal ALD the co-reactants are often water, oxygen or ozone. For depositing iridium or iridium oxide films, high temperature, mostly over 200 °C is necessary to achieve film growth [8, 9] . In plasma enhanced ALD (PE-ALD) the co-reactant is replaced by a plasma, which provides the reaction energy. Using plasma, a coating at moderate temperature is possible, whereas the substrates to be coated are not exposed to a high thermal stress. Thus, this process is favourable for polymer-based neurotechnological implants.

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In this work, a PE-ALD process is developed with the aim to form iridium oxide (IrO_x) thin films using the (Methylcyclopentadienyl) (1,5-cyclooctadiene) iridium(I) precursor ((MeCp)Ir(COD)) and oxygen plasma as a co- reactant at low temperatures. Because of the low melting point of the precursor of 35-40°C low deposition temperatures are possible. To the best of our knowledge, no iridium oxide PE-ALD processes have been reported using this precursor prior to this paper. Hämäläinen et al. have used the (MeCp)Ir(CHD) precursor to deposited iridium oxide films with ozone as a co-reactant at low temperatures [10] and Kim et al. have used the (EtCp)Ir(COD) precursor to deposit iridium and iridium oxide films at 230 °C up to 290°C by using oxygen as the co-reactant [11]. By varying the pulse time of the precursor, the suitability of this precursor for the ALD process will be investigated.

2 Material and Methods

The iridium oxide layers were deposited in a plasma enhanced atomic layer deposition (PE-ALD) process with the ALD reactor "myplas III ALD" (Plasma electronic GmbH, Germany) using the precursor (MeCp)Ir(COD) and oxygen plasma as the co-reactant at a temperature of 110 °C. The precursor was delivered into the reaction chamber in vapor draw and the oxygen gas was supplied over a showerhead, which also serves as an RF-electrode for producing the plasma. Nitrogen 5.0 (Linde, Germany) was used as the purge gas. The purge time after the precursor pulse was 1 s, and after the oxygen plasma 3 s. The precursor pulse time was varied from 0.5 seconds to 5 seconds to determine the ALD window. As substrates, 10 x 10 mm^2 silicon wafers (100), with a native oxide layer were used.

Film thickness was measured using the M-2000F^{TM} spectroscopic ellipsometer (J. A. Woollam Co., Inc., USA, Nebraska). The spectroscopic graphs were acquired with an angle of incidence of 65° at a wavelength from 375 nm to 1000 nm. The graphs were evaluated and the thicknesses of the layers were determined using the CompleteEASE 5.19 software (J. A. Woollam Co., Inc., USA, Nebraska). To describe the measured layers, a mathematical model was created using silicon as the substrate material and a B-spline model describing the iridium oxide layers.

The deposited layers were studied using atomic force microscopy (NanoSurf CoreAFM, Germany) on an area with 500 x 500 nm^2 under ambient air in tapping mode. The measured data were analyzed and interpreted using MountainsSPIP®Expert software (Digital Surf, France).

The deposited IrO_x films were characterized by energy-dispersive X-ray microanalysis technique (EDX), using the Phillips ESEM XL30 for this purpose. The samples were tilted by 15°. The acceleration voltage was 6 kV.

3 Results and discussion

3.1 ALD-Window

Figure 1 shows the dependence of the measured film thickness in respect of the pulse length of the (MeCp)Ir(COD) precursor at 110 °C. For the investigation for the suitability of the precursor to perform ALD, 500 deposition cycles were carried out. No pressure raise was detected when the precursor was pulsed into the chamber. Through both purging steps and the plasma step, the pressure did not exceed 5 Pa. The pulse length was varied from 0.5 s up to 5 s, and the oxygen plasma pulse was fixed to 2.75 s with a power of 200 W. The deposition rate was saturated at a thickness of approximately 33 nm after 500 cycles, when the pulse length exceeds 2 s. The coating follows ALD characteristics and a self-limiting growth. No increase in film thickness was observed with pulse times longer than 2 seconds. The growth per cycle (GPC) was calculated to 0.66 Å/cycle.

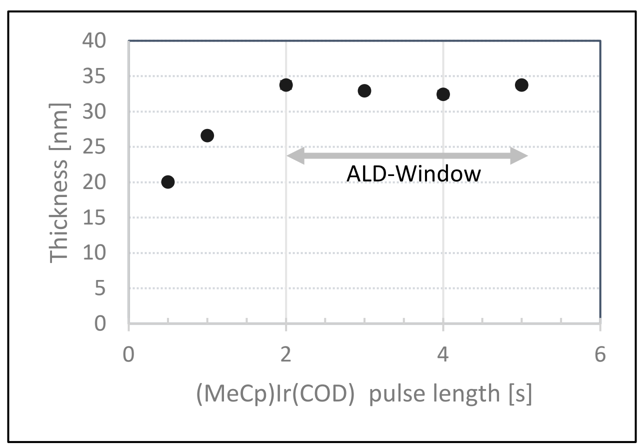

Figure 1: Thickness of iridium oxide thin films on silicon oxide wafers as a function of the precursor pulse length.

3.2 EDX Analyses

In the previous section it was shown that a layer growth occurs, and that the growth is self-limiting. To determine the elemental composition of the deposited film and validate that

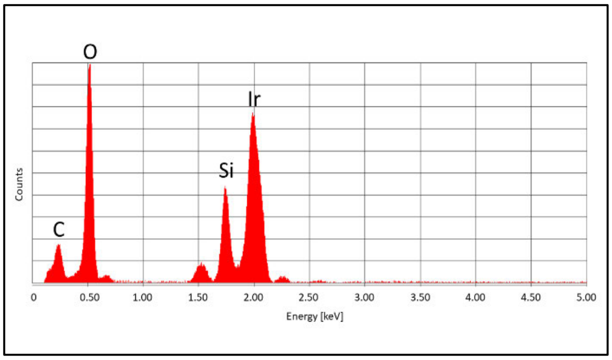

Figure 2: EDX spectrum of the silicon wafer coated with iridium oxide (IrO_x)

the film consists of IrO_x, EDX analyses were carried out. The analysis of thin films requires a low accelerating voltage (a few keV) which still must be high enough to excite the elements of interest. A rule of thumb is that three times the excitation energy should be chosen as the accelerating voltage [12].

In Figure 2 the EDX-spectrum of the layer is shown. The three main peaks represent the elements oxygen Kα at 0.525 keV, silicon Kα at 1.740 and iridium Mα at 1.980 keV. Carbon Kα at 0.277 keV as an impurity was also detected.

A quantified analysis of the EDX spectrum showed a ratio between oxygen and iridium of close to 2:1. Iridium is present with 24.59 at% and oxygen with 44.01 at%. Although this is not exactly a 2:1 ratio, Kim et al. [11] reported in their experiments of depositing iridium oxide layers by ALD with the precursor (EtCp)Ir(COD), that a pure iridium layer is formed at the interface between the iridium oxide layer and silicone surface, which may be responsible for the shift in the ratio. A small amount of oxygen is contained in the native oxide layer onto of the silicone substrate. The carbon impurities were quantified to 8.90 at%. It has to be clarified in further experiments, if the carbon is related to the electron beam exposure in the SEM or is related to carbon being incorporated in the sample during deposition. Taken together, these analyses points to that deposition of IrO_x was successful, a promising result pointing to ALD as a possible future technique for deposition of IrO_x films at low temperature.

3.3 AFM Images

The AFM image in Figure 3 shows the surface of the iridium oxide films, deposited with a precursor pulse length of 3 s. The datapoints were levelled and a 3D representation was generated. The average square height (S_q) was calculated over the entire area and is shown in Table 1. A S_q of 0.6 nm describes a smooth surface, and indicates that the coating is conformal, which also expected as the coating represents the smooth surface morphology of the silicon substrate

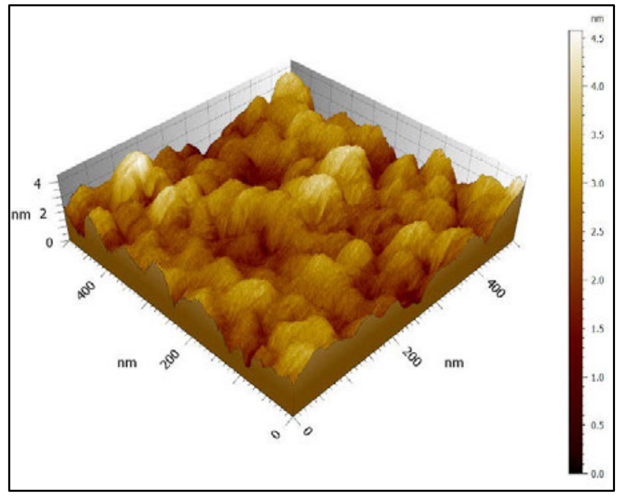

Figure 3: AFM Image of IrOx films deposited with a precursor pulse length of 3 s

underneath. For neurotechnological microelectrodes a rough surface is often desirable to increase the capacitive coupling with the electrolyte and lower the electrochemical impedance. A highly conformal deposition technique, such as ALD, and therefore a highly conformal film, will allow the morphology of a rough substrate to be replicated [13]. Thus, the electrode substrate can be enlarged by other roughening techniques, leading to a larger interaction surface, and ALD can be used to functionalize the rough surface further with IrO_x.

Table 1: Heights Parameters calculated out of the AFM-data with the MountainsSPIP®Expert software

Parameter	[nm]
S_q (Average square height)	0.6
S_P (Maximum tip height)	2.1
S_V (Maximum recess depth)	2.3
S_Z (Maximum height)	4.5

4 Conclusion

Iridium oxide thin films were successfully deposited on silicon wafers using the PE-ALD method at 110 °C. Through varying the pulse length of the precursor limited growth could be observed. Thus, a process for depositing in the so called ALD-window (surface-controlled growth) could be found. A growth per cycle of 0.66 Å/cycle was calculated, which is lower than the GPC of 1.5 Å/cycle of a similar precursor, (EtCp)Ir(COD) at 290 °C. However, the pulse length of the precursor and also the co-reactant (mixture of oxygen and argon) was 10 s [11]. Using EDX-analysis, the iridium oxide films were identified. AFM images revealed a smooth surface with a S_q of 0.6 nm.

5 Outlook

In this work, the objective was to validate the principal ability of the precursor to be used for ALD. The experiments could be performed with a very small precursor quantity of 1 g. Due to the promising results, the process will be transferred to a larger PE-ALD-system (FlexAl, Oxford Instruments, England). On this facility, a finer adjustment of process parameters is possible, allowing for more process variations.

For further experiments, the electrochemical properties of the coatings will be investigated. The measurement methods of cyclic voltammetry and electrochemical impedance spectroscopy will be applied. The coatings will also be measured using the Kelvin technique (four-probe method) to determine the sheet resistance.

Subsequently, the coatings will be deposited on neurotechnological probes to verify the performance of the iridium oxide microelectrodes coatings under physiological conditions and in standardized performance tests [14].

Author Statement

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