Increased Charge Storage Capacity of Titanium Nitride Electrodes by Deposition of Boron-doped Nanocrystalline Diamond Films

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Abstract: The aim of this study was to investigate the feasibility of depositing a thin layer of boron-doped nanocrystalline diamond (B-NCD) on titanium nitride (TiN) coated electrodes and the effect this has on charge injection properties. The charge storage capacity increased by applying the B-NCD film, due to the wide potential window typical for B-NCD. The impedance magnitude was higher and the pulsing capacitance lower for B-NCD compared to TiN. Due to the wide potential window, however, a higher amount of charge can be injected without reaching unsafe potentials with the B-NCD coating. The production parameters for TiN and B-NCD are critical, as they influence the pore resistance and thereby the surface area available for pulsing.

1 INTRODUCTION

Neural stimulation with implantable electrodes is used for many applications (Zhou, 2009). The surface to area ratio of these electrodes can be increased by applying a porous coating (Cunha, 2009; Specht, 2007). This gives the electrodes the following advantages: fast stabilization of the open circuit potential (OCP), making stimulation and sensing with the same electrode possible (Specht, 2007), high charge injection capacity, which allows for electrode miniaturization (Cogan, 2008; Zhou, 2009).

Titanium nitride coatings can be made smooth or porous by controlling deposition parameters, such as nitrogen (N_2) flow. At a low N_2 flow a smooth Ti-rich metallic film can be obtained. Increasing the flow results in a smooth (stoichiometric) TiN film and further increasing the N_2 flow results in a porous (over-stoichiometric) N-rich film (Cunha, 2009). The pores extend deep into the coating, resulting in a high surface to area ratio and a high charge storage capacity (CSC) (Cunha, 2009; Norlin, 2005).

An increased amount of nitrogen in the coating, however, also results in increased dissolution rates and oxide thickness when high anodic potentials are reached (Cunha, 2009). In addition, higher potentials were observed when applying stimulation pulses using implanted TiN electrodes (Meijs, 2015), which may compromise safety during electrical stimulation. It is thus advantageous to apply an additional coating to improve the corrosion resistance and *in vivo* electrochemical properties.

Boron-doped nanocrystalline diamond (B-NCD) was selected, to combine its be mechanical stability, biocompatibility (Tang, 1995; Garrett, 2015) and corrosion resistance (Hupert, 2003) with the large sufe to area ratio of TiN (Cunha, 2009). B-NCD further has metal-like electrical properties and a wide safe potential window (Garret, 2012; Meijs, 2013). In addition, B-NCD is fouling resistant (Hupert, 2003), which may decrease the electrode potential during pulsing with implanted electrodes.

2 METHODS

2.1 Electrode Fabrication

The TiN coatings were deposited on the tip of 16 Ti6Al4V electrode pins (6 mm^2) by reactive DC

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magnetron sputtering using an industrial CC800 coating unit (CemeCon AG, Germany). Sputtering was done from four Ti targets (88 x 500 mm^2) with 99.5% purity in an Ar/N_2 mixture atmosphere. The N_2 flow was varied from 120 to 300 sccm, while the Ar flow was constant. The deposition time was varied in order to obtain different coating thicknesses.

Titanium-nitride electrodes were then coated with B-NCD using an Astex AX6500 microwave plasma enhanced chemical vapor deposition system. The electrodes were first immersed in a 0.33 g/L solution of diamond nanoparticles (3.8 ± 0.7 nm) from Shinshu University to seed the surface for diamond growth. Hydrogen gas with an addition of 1% CH4 was added to the chamber at a total flow rate of 500 sccm. Tri-methyl boron (TMB) was added to the gas as the dopant source, at boron to carbon concentrations of 10,000ppm. The plasma was maintained at a temperature of ~750 °C by using a pressure of 25 torr and a microwave power of 2500 W for the plasma.

2.2 Electrochemical Measurements

All electrochemical measurements were carried out in a 3-electrode set-up, using the TiN/B-NCD pins as working electrodes (0.06 cm^2), a platinum foil counter electrode (50 cm^2) and a Ag|AgCl reference electrode (1.6 cm^2). Measurements were performed in Ringer solution at room temperature.

The impedance spectrum was measured from 0.1 Hz-100 kHz, 5 points/decade using a sinusoidal measurement current of 5.0 µA. Impedance spectroscopy was performed using Solartron, Model 1294 in conjunction with 1260 Impedance/gain-phase Analyzer (Solartron Analytical, UK).

Cyclic voltammetry was performed by cycling the electrode potential between the water window limits. These limits were determined by increasing and decreasing the electrode potential until an exponentially increasing current was observed using a sweep rate of 0.05 V/s. Measurements were made at 0.05, 0.1, 0.5 and 1.0 V/s; 10 cycles were recorded at each sweep rate. The cathodic charge storage capacity (CSC) of the electrodes was found by calculating the surface area under the 0 A axis.

Voltage transient measurements were made using a cathodic-first bipolar symmetric current pulse with an inter-phase, during which no current was applied. Each phase had a phase width of 200 µs and the duration of the inter-phase was 40 µs. For analysis of the voltage transients, the OCP was set to 0 V and the IR drop was subtracted. The IR-drop was calculated for each phase by subtracting the potential at 20 µs after pulse cessation from the last data point of the respective phase. The pulsing capacitance (C_{pulse}) was calculated for each pulse using the following equation:

$$I_{stim} = C_{pulse}\frac{dV}{dt} \quad (1)$$

where I_{stim} is the stimulation current and $\frac{dV}{dt}$ is the slope of the last 90% of the cathodic phase of the voltage transient.

Cyclic voltammetry and voltage transient measurements were performed with VersaSTAT 3 potentio- galvanostat (Princeton applied research, USA).

3 RESULTS

Two of the pins were coated with a smooth (stoichiometric) TiN coating, while all others were over-stoichiometric and displayed an open pyramidal columnar structure. The surface to area ratios of the porous electrodes ranged from 89 to 295, calculated by dividing the CSC of the porous coatings by the CSC of the smooth coating. The coating thicknesses varied with N_2 flow and deposition time (table 1). Diamond films were deposited on the TiN coatings. These films had uniform coverage on the TiN with grain size of ~50nm (Fig. 1). The film thickness was measured using silicon substrates coated under the same conditions, which gave a film thickness on the order of the grain size, around 50-70nm.

Table 1: Deposition parameters and coating thicknesses for porous TiN coatings.

N_2 flow (sccm)	Deposition time (10^3 s)	Coating thickness (µm)	Ref. nr.
120	27.5	5.2	45
180	10	2.1	46
180	27.5	6.3	52
180	60	13.1	54
240	10	2.0	47
240	27.5	4.6	53
300	27.5	1.6	55

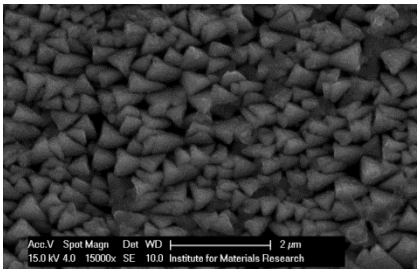

Figure 1: SEM of B-NCD coated TiN electrode (ref. 52).

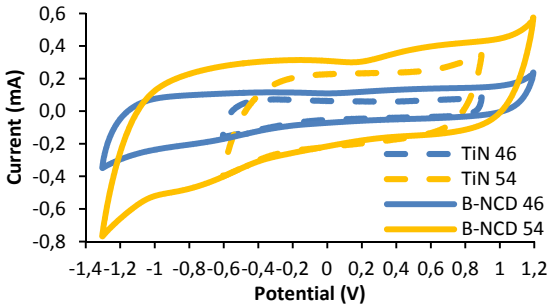

Figure 2: The CV of the B-NCD coated TiN electrodes had wider safe potential limits, which increased the CSC.

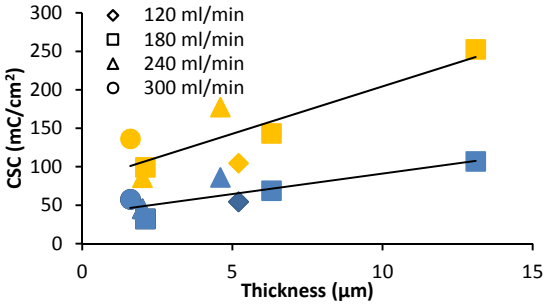

Figure 3: CSC increased linearly with coating thickness. The blue markers correspond to TiN (r^2=0.71) and red markers to B-NCD (r^2=0.74).

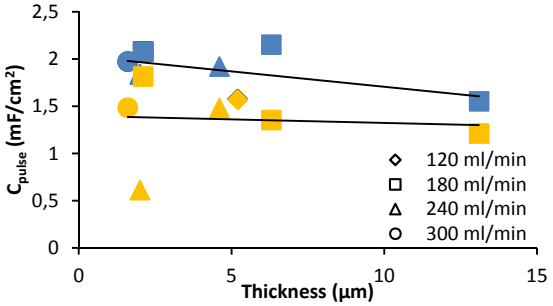

Figure 4: C_{pulse} did not increase with coating thickness. The blue markers correspond to TiN (r^2=0.32) and red markers to B-NCD (r^2=0.01).

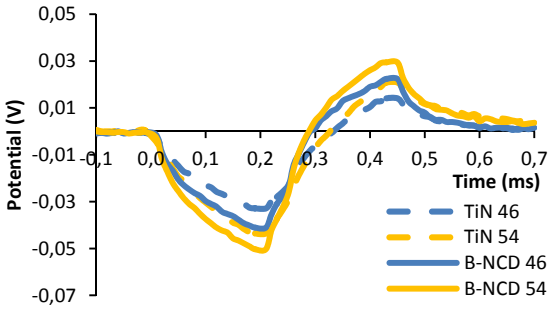

Figure 5: C_{pulse} of B-NCD coated TiN electrodes was decreased compared to uncoated TiN. This caused a steeper voltage rise and greater electrode potentials.

The water window was -0.6 V – 0.9 V (Ag|AgCl) for TiN and -1.3 V – 1.2 V for B-NCD. Due to the wide potential window typical for B-NCD, the CSC of the B-NCD coated electrodes was 2-3 times larger than the CSC of TiN electrodes (Fig. 2). Furthermore, the CSC of both B-NCD and TiN electrodes increased with increasing coating thickness (Fig. 3). The CSC of B-NCD coated electrodes was consistently higher than the CSC of TiN electrodes

The impedance magnitude for the B-NCD and the TiN electrodes decreased with increasing thickness. All B-NCD coated electrodes had a higher impedance than without the B-NCD coating.

Contrary to the CSC, C_{pulse} did not increase with coating thickness. The trend lines even have a slightly negative slope for both TiN and B-NCD electrodes. Also, C_{pulse} of the B-NCD coated electrodes was lower than C_{pulse} of the corresponding TiN electrodes (Fig. 4). Fig. 5 shows that a lower C_{pulse} resulted in in higher electrode potentials. The potential limit for B-NCD, however, is higher than for TiN.

The highest CSC and lowest impedance magnitude for TiN with and without B-NCD coating were obtained using the thickest coating (ref. nr. 54). The main parameter that influenced the coating thickness was the coating time. The highest C_{pulse}, however, was obtained with thinner coatings.

4 DISCUSSION

We have coated 16 TiN electrodes with various high surface to area ratios with a thin layer of B-NCD. Depositing a B-NCD thin film on a porous TiN substrate improved the previously reported electrochemical performance of the B-NCD electrodes (Garrett, 2012; Meijs, 2013) to a level that is comparable to porous TiN electrodes.

The TiN electrodes had a high surface to area ratio (89-295), which resulted in a high CSC and low impedance magnitudes. A thicker coating resulted in a higher CSC due to the increased surface to area ratio. This suggests that pores extend into the entire depth of the coating (Cunha, 2009; Norlin, 2005). Depositing B-NCD on top of the TiN further increased the CSC. There was a linear relation between the TiN CSC and the B-NCD CSC (fig. 6). This indicates that the B-NCD coating did not block the pores, but covered the inner surface of the TiN columns without obstructing the pores.

The highest C_{pulse} for TiN electrodes was found for a 6.3 µm thick coating, while the lowest C_{pulse} for B-NCD coated electrodes was found for a 2.1 µm thick coating. Both TiN coatings were produced un-

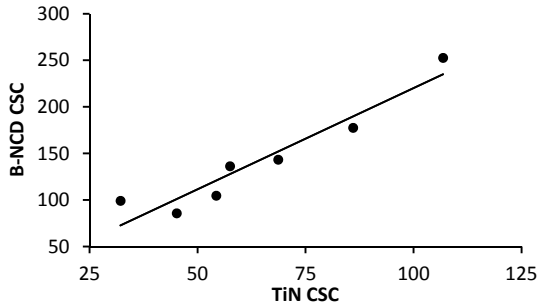

Figure 6: There is a linear relationship between the CSC of TiN and B-NCD coated TiN electrodes (r^2=0.91).

der similar conditions and the increased thickness was achieved by increasing the coating time. As the B-NCD coating is added, however, the pores of the electrodes become narrower. This increases the pore resistance and decreases the pore depth that can be used under pulsing conditions (Cogan, 2008). This makes it less advantageous for electrical stimulation purposes to increase the coating thickness beyond a certain level. For TiN electrodes, the optimal thickness is between 6.3 and 13.1 µm, while for B-NCD coated TiN electrodes it is between 2.1 and 5.2 µm with the settings used in this study. A thicker coating may be more advantageous, if the pores are wider without comprising mechanical stability.

The electrochemical properties of the B-NCD coated TiN electrodes are far better than those of conventional B-NCD electrodes (Garret, 2012; Meijs, 2013). This is due to the large surface to area ratio gained by the TiN on which B-NCD was grown. B-NCD with a high surface to area ratio was also made by growing diamond on carbon nanotubes, resulting in great improvements in impedance and CSC (Piret, 2015). The CSC of the current electrodes is, however, 3-10 times higher than the CSC of B-NCD coated carbon nanotube electrodes.

Although C_{pulse} is decreased for B-NCD coated electrodes compared to TiN, it is important to view this result in the light of wide safe potential window of B-NCD (Garrett, 2012, Piret, 2015). The decrease in C_{pulse} after depositing B-NCD ranged from 67% to less than 1%, while the cathodic potential limit was more than doubled (-0.6 V vs Ag|AgCl for TiN and -1.3 V vs Ag|AgCl for B-NCD). This means that the amount of charge that can be injected without reaching unsafe potentials is doubled by applying a B-NCD coating on top of a porous TiN coating.

In order to achieve increased charge injection (Q_{inj}), the production parameters are of critical importance, as the extra coating increases the pore resistance, which may deteriorate Q_{imj}. This study suggests that specific deposition parameters are optimal for stimulation electrodes, as increased thickness and N_2 flow only result to a certain extent in larger C_{pulse} and Q_{inj}. These settings, however, also depend on the thickness of the diamond film.

5 CONCLUSIONS

The charge storage and charge injection capacity of porous TiN electrodes can be improved by adding a B-NCD coating. We further expect that the B-NCD coating will improve the corrosion and fouling resistance of porous TiN electrodes.

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