33rd Annual International Conference of the IEEE EMBS
Boston, Massachusetts USA, August 30 - September 3, 2011

In Vitro Study of Titanium Nitride Electrodes for Neural Stimulation

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Abstract— **For neural stimulation, reliable high density charge transfer into tissue is required. One electrode material for these applications is titanium nitride (TiN). In this paper, a method for lifetime analysis of TiN electrodes is discussed. Our method significantly differs from open literature. The tests were run for much longer durations. Special attention was paid to the optical appearance and electrode voltage response to different input current pulses. According to our investigations, TiN electrodes are able to deliver at most 0.2mC/cm^2 charge density for square shaped electrodes with 50µm x 50µm dimensions in safe operation, which is less compared to previous reports. The safe operation window for TiN was confirmed to be ±1V in terms of electrode potential with the counter electrode considered as reference. We found that the shape of the waveform does not affect electrode lifetime. Our measurements show that rectangular voltage waveforms inject the most amount of charge into the electrodes compared to other shapes. This makes rectangular electrode voltage signals optimal for highest charge injection at a given lifetime. In our case with square electrodes, the absolute electrode potential is found to be the more important parameter in electrode lifetime, compared to Helmholtz capacitor voltage drop.**

Index Terms **— TiN, electrode, lifetime, impedance spectroscopy**

I. INTRODUCTION

SAFETY and biocompatibility are among the most important factors in a prosthetic neural stimulator. In recent years, TiN has undergone much experimental analysis to determine if it could safely be used for a neural prosthesis system. TiN is a standard material in integrated circuit fabrication, so using it as an electrode material does not necessarily require new methods for fabrication [1].

In general, one of the most important parameters regarding the application of a material for fabricating electrodes is the safe operation voltage in which no electrode damage occurs [2]. Table 1 lists a summary of the literature regarding different parameters of TiN electrodes. In this paper, a novel method for lifetime analysis of TiN electrodes is discussed.

TABLE I
COMPARISON BETWEEN DIFFERENT TIN ELECTRODE PARAMETERS FROM DIFFERENT PAPERS

Paper	Charge Injection Limit	Safe Voltage Window	Interface Capacitance
[3]	-	-	0.035F/cm^2
[4]	2.2 to 3.5 mC/ cm^2	-1V to +1.2V	0.5 to 1mF/cm^2
[6]	-	-	10mF/cm^2
[7]	23 mC/ cm^2	-	-
[8]	1 mC/ cm^2 CSC_C=250µC/ cm^2	-0.9V to +0.9V	-
[9]	950µC/ cm^2 and 550µC/ cm^2 for cathodic and anodic pulses	-0.6V to +0.8V	-
[10]	-	-0.3V to +0.6V	-

II. FABRICATION PROCESS OF MICRO ELECTRODE ARRAYS (MEAS)

The microelectrode array (MEA) is manufactured using thin film lithography on a float glass substrate. Gold lines are patterned with a lift-off technique on the surface of the substrate. The metal lines are covered with a polyimide insulation layer. A hard mask is used to remove the polyimide at the electrode sites and over the conduction pads. The titanium nitride electrodes are patterned in a subsequent lift-off process. The profile of one electrode is shown in Fig 1.

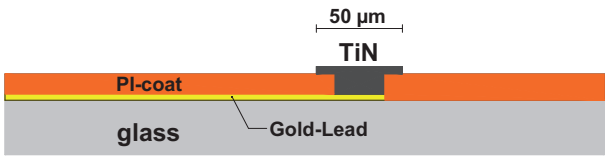

Fig. 1. Profile of MEA

III. Experimental Setup

For our experiments, a test arrangement was designed including a laptop, an NI-6259 multifunctional board, special electrode driving circuitry and several MEAs. The whole system is controlled by a LabVIEW computer program. Fig. 2 shows the test setup block diagram.

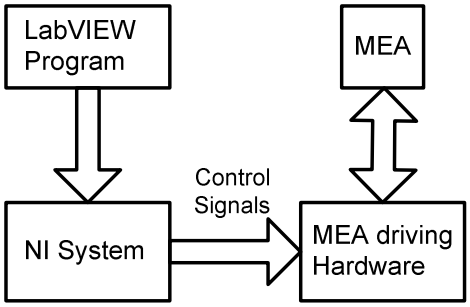

Fig. 2. Block diagram of the experiment setup

The MEA includes fields of 64 TiN electrodes, each being 50 µm x 50 µm in size. Groups of 4 electrodes are connected to one pad each. The MEA is coated by polyimide (PI) layer for protection.

The functionality of the electrode driving circuit is shown in Fig. 3. A current source provides biphasic signals with 0.3ms cathodic pulse length, 0.5ms anodic pulse length and a period of 3ms.

16 electrodes were connected in parallel to one driving circuit, thus the measurements here correspond to 16 electrodes. A high quality of fabrication process ensures homogeneity among electrodes. Throughout all the tests, the medium was PBS (phosphate buffered saline). The counter electrode was always connected with the system ground. The counter electrode area was much bigger than the working electrodes, ca. 0.2cm^2.

Two different waveforms were generated. In the triangular case, the magnitudes for the cathodic and anodic current pulses were adjusted to generate nearly biphasic triangular voltage waveforms for the electrode voltage V_E shown in Fig. 3 (fixed current pulses, Fig. 4). In the biphasic rectangular voltage waveform case, current limit was set very high. Here the electrode voltage looked approximately rectangular. For both triangular and rectangular waveforms, the voltage peaks were set by the adjustable voltage limiter. After the anodic pulse there was an electrode discharge via a switch having an on-resistance value of 1kΩ. We assume that the electrode potential plays the major role in electrode lifetime [8], so the discharge current was not controlled and investigated.

During the lifetime tests, every few days the electrode voltages and currents were measured, electrode photographs were made, and impedance spectroscopy graphs were made by a VersaSTAT 4 potentiostat.

The last was found to be less significant. There were numerous cases in which we could already observe an optical change in electrode's appearance or electrode voltage signal form but no change appeared in the impedance spectrum. The reason is explained later.

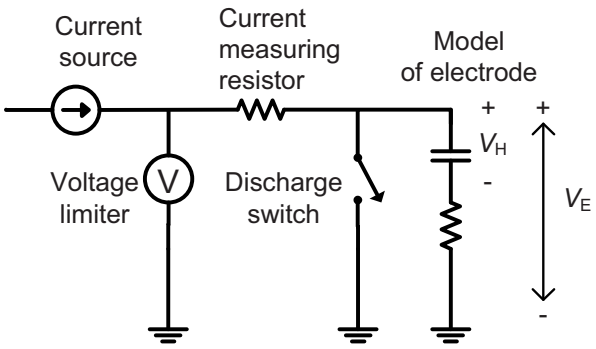

Fig. 3. Equivalent circuit diagram of the driving circuit

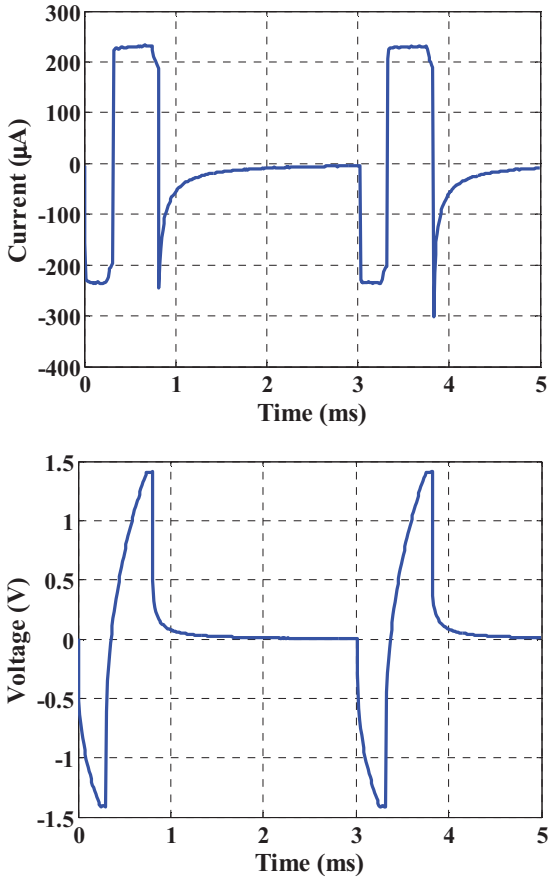

Fig. 4. Measured electrode current and voltage for 16 electrodes for the case of a biphasic triangular ±1.4V voltage waveform.

IV. Experiment Results

Different voltage boundaries from ±0.5V to ±1.4V were tested in the lifetime tests. Totally 25 of such tests were done. We found out that at voltages up to ±1V, the electrode damage is negligible during lifetime tests as long as 2 months. In the

experiments at the bigger voltage limits of ±1.1V, electrode damage was observed after only 1 week. This includes both the electrode appearance and the measured injected charge per current pulse. The tests were run at most for 2 months, assuming that no change would occur after that. If there was already a significant change, the experiment was stopped. The electrode damages apparently did not depend on the electrode potential waveform, i.e. triangular or rectangular. Table 2 summarizes the most important accomplished experiments and the corresponding results.

Fig. 5 shows the darkening of the active electrode surfaces after one week due to oxidation. Here the electrode voltage was a triangular ±1.4V voltage waveform at the beginning. Fig. 6 shows the measured output signals after one week. Here, the originally triangular electrode voltage waveform (Fig. 4) deforms and also a drop occurs at the end of the current pulse (originally rectangular). This indicates that an electrode oxidation has occurred, reducing the electrode capacitance. So while the output current of the current source remains constant, the electrode voltage reaches the adjusted voltage limits of the voltage limiter faster. After this a part of the injected current flows into the voltage limiter and the electrode current begins to drop.

TABLE II
A SUMMARY OF THE ACCOMPLISHED EXPERIMENTS AND THEIR RESULTS

Experiment	Experiment Length	Optical change	Decrease in Charge Inj.
±0.5V	2 Months	Nothing	Nothing
±1V	2 Months	Very little	10%
±1.1V	1 Week	Considerable	15%
±1.2V	1 Week	Considerable	20%
±1.4V	1 Week	A lot (Fig. 5)	25%

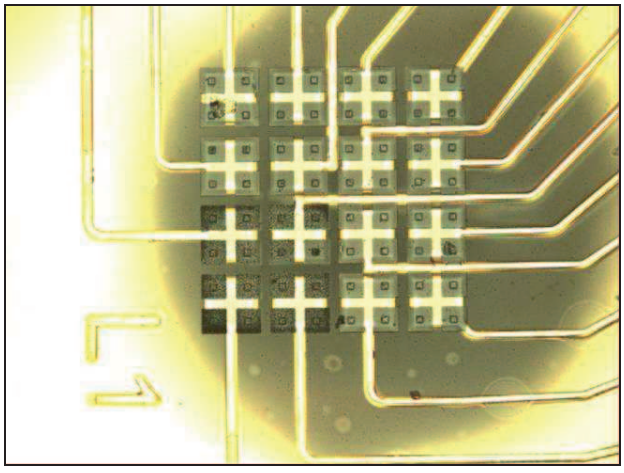

Fig. 5. Active electrode darkening effect with ±1.4V voltage boundaries. The active electrodes are on the bottom left corner. The others were not driven.

As mentioned above these criteria were more reliable than the impedance spectroscopy diagrams. For the above case, little change was seen for the measured impedance spectrum of the 16 electrodes. This was observed many times, exhibiting the weakness of impedance spectrums as a determining factor. We explain this as follows: In impedance spectroscopy, a small signal sinus voltage (in our case having 10mV amplitude) is used, but this cannot cover all the electrode properties. Different electrode parameters change strongly nonlinearly with electrode voltage, so they are different for higher voltages, in our case as high as ±1.4V. Therefore our transient electrode voltage and current measurement offers a more reliable method.

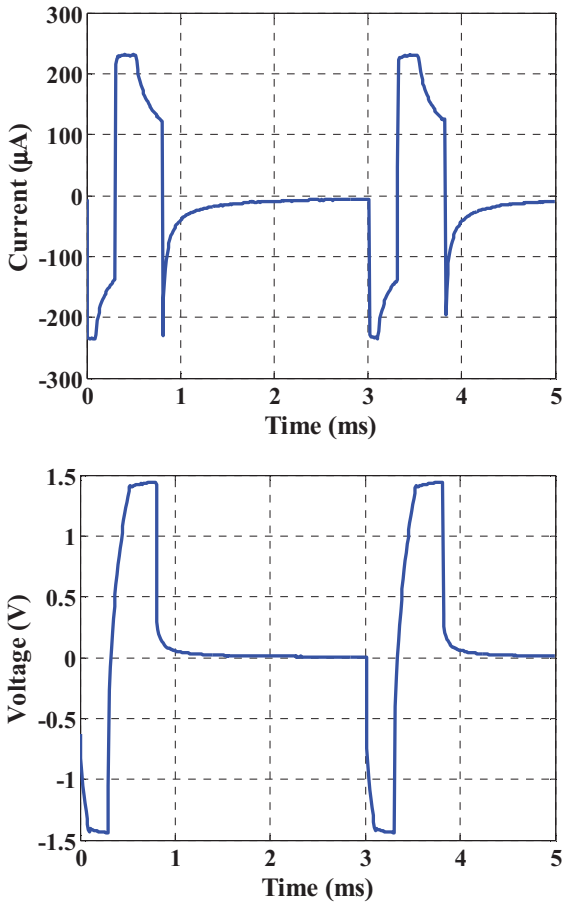

Fig. 6. Above: Output current waveform shows a current drop, a sign indicating the electrodes were oxidized. At the beginning of the test the current pulse was rectangular (Fig. 4). Below: Corresponding output voltage waveform begins to be more rectangular. At the beginning it was triangular.

The maximum charge injection capacity of TiN electrodes, in our case, measured with ±1V voltage limits, is 5nC per electrode, equaling 0.2mC/cm^2.

We observe that in our case with square electrodes, absolute electrode potentials (counter electrode is grounded) are more important for lifetime than electrode's Helmholtz capacitor voltage drop. [12] So we find the electrode potential of ±1V as the safe operation range.

To estimate the voltage drop on the Helmholtz capacitor, we use a first order electrode model comprising just a capacitor and a resistor. The model parameters are derived from the measured transient waveforms while applying a square wave voltage of ±1V to a set of 16 electrodes. The resulting

electrode current is shown in Fig. 7. We can estimate the time constant for cathodic and anodic pulses, respectively. TiN Helmholtz capacitor has a nonlinear characteristic [9], which we neglect in our first order model. We found values of approximately 2kΩ and 110nF. Subtracting the 470Ω of the current measurement resistor we obtain 1.53 kΩ for 16 electrodes. Thus the spreading resistance per electrode is 24kΩ and the electrode capacitance equals 6.87nF.

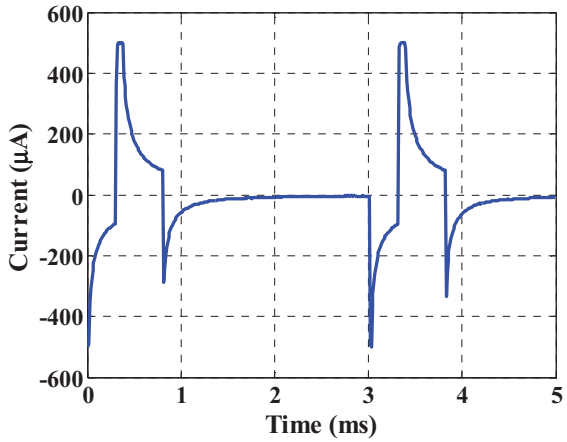

Fig. 7. Electrode current in response to a ±1V biphasic square voltage on the electrode.

With this model, and using simple circuit simulations, we obtain voltage amplitudes of -590mV to +550mV on the Helmholtz capacitance (V_H, see Fig. 3) in the ±1.1V triangular electrode voltage (V_E) case, and -740mV to +810mV in the rectangular ±1V case. As said before, we have a far less lifetime for ±1.1V triangular voltage case compared to the rectangular ±1V one. This shows that not the Helmholtz capacitor voltage drop, but the absolute electrode potential is the critical parameter for electrode lifetime. This confirms the results in [8],[12]. One explanation might result from the non uniform current distribution that leads to larger potentials at the edge of the electrodes [11]. For a porous material like TiN, there is an additional non uniformity of potentials through the thickness of the electrode coating [8].

We conclude that rectangular electrode voltage waveforms provide highest charge transfer for a given lifetime.

V. Conclusion

With a test setup developed at the University of Ulm, we were able to find a safe operating range for TiN electrodes in terms of voltage of ±1V. This is slightly higher than previously reported ±0.9V [8]. We also found that the voltage waveform does not play a major role, confirming previous reports like [12] which claim the absolute electrode potential is the more important parameter in electrode safety, compared to Helmholtz capacitor voltage drop. We saw that the method of impedance spectroscopy does not offer a reliable way to assess electrode deterioration in our case, so we chose optical investigation together with measuring the output voltage and current waveforms.

We found that with a maximum charge injection capacity of 0.2mC/cm^2 and an operation range of maximally ±1V, the electrodes experience negligible changes for test durations as long as 2 months. For voltages of equal to or larger than ±1.1V there are significant changes after one single week. For highest injected charge, rectangular electrode potential waveforms are considered as optimal.

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