Deposition and Characterization of Ruthenium Films for Neural Electrodes

Diana Wu
Chemical Engineering and Biology, Massachusetts Institute of Technology

Emily Hoffman
Materials Science and Engineering, Northwestern University

NNIN iREU Site: Interuniversity Microelectronics Center (imec), Leuven, Belgium
NNIN iREU Principal Investigator: Dr. Hercules P. Neves, imec, Leuven, Belgium
NNIN iREU Mentor: Dr. Aleksander Radisic, imec, Leuven, Belgium
Contact: dianatwu@gmail.com, eh@u.northwestern.edu, herc@imec.be, radisic@imec.be

Abstract:

Neural probes are used to stimulate neurons or record electrical signals, which can be instrumental in understanding the neural network and treating disease. Platinum and iridium are currently used as the electrode material, but ruthenium has promising properties. It is important that materials have high charge storage capacity and low impedance. We investigated the deposition of ruthenium oxide films on gold, titanium nitride, platinum, and atomic layer deposited ruthenium. The samples were characterized using cyclic voltammetry and impedance spectroscopy to predict their performance for neural probe applications.

Introduction:

Neural probes interface electrical stimulation with biological tissue such as neurons. These probes can be used to stimulate or to record the activity of the neurons. Applications of the probes include deep brain stimulation for Parkinson's disease, epilepsy, and depression [1, 2].

Neurons can be stimulated by creating a functional response by depolarizing membranes of excitable cells through the injection of current from the probe. This creates a flow of ionic current between two or more electrodes, one which is near tissue. Neural activity can also be recorded by micro-probes by measuring the potential created by neuron membrane depolarization. Current probes are made of platinum (Pt), iridium oxide (IrO_2), and titanium nitride (TiN) [1, 3, 4].

For stimulation, probes must be able to send a charge-balanced waveform to avoid damage to the electrode and surrounding tissue [1]. Chemically, probes must be bio-compatible. Any reactions that occur at the electrode surface must not release harmful molecules into the body or degrade the electrode so that performance is affected. Neural probes should be small in size to be less intrusive in the brain tissue [1].

The goal of this project is to improve the electrical performance of neural probes by plating ruthenium (Ru) metal onto possible probe substrates. It is worthwhile to investigate the use of Ru because it has more reduction-oxidation states and could provide a better interface with tissue. An increased number of states may correspond to a greater charge injection, which would be useful for brain stimulation. Ruthenium also shares similar biocompatibility and corrosion resistance properties to other currently successful materials [5].

Deposition Methods:

Electrochemical deposition is selective and a very small area can be plated. In this report, electrochemical deposition was used to deposit Ru on multiple substrates to investigate its usefulness for improving neural probes.

To deposit Ru onto different substrates, a three probe setup was used with a potentiostat (Autolab Booster 20 A). A Ag|AgCl reference electrode and platinum counter electrode were used. Ruthenium was deposited using constant voltage deposition, and constant current deposition at varying magnitudes and for various times. Two electrolytes were investigated: $(Ru(NO_2))_2(SO_4)_3$ and $RuCl_3$. In some samples, the electrolyte was heated to approximately 60°C to increase the kinetics of the solution.

Several substrates were used for deposition: gold (Au), platinum (Pt), titanium nitride (TiN) and titanium nitride treated with hydrofluoric acid (TiN HF). Atomic layer deposited ruthenium (ALD Ru) was used as a control.

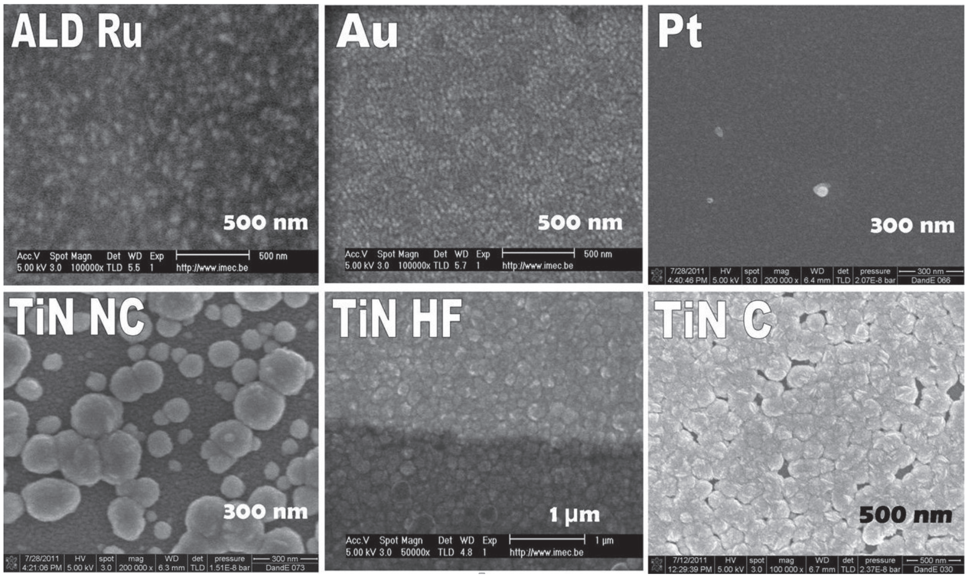

Figure 1: SEM images of the primary samples investigated.

Deposition Results and Discussion:

The electrochemical plating process was used to deposit a film of Ru on the various substrates. After deposition, the samples were visually inspected to determine the continuity of the film and the overall quality. Visually, the continuous samples appeared shiny, while non-continuous films were milky and spotted because of the clustered of nucleated Ru. The other continuous samples were silver to purple in color and appeared smooth.

To test for initial adherence to the substrate, a tape test was performed. All samples remained bonded to the substrate after tape was adhered and pulled from the ruthenium film, showing electrochemically plated Ru has sufficient adhesion properties.

Promising samples were imaged using scanning electron microscopy (SEM) to evaluate the grain size and continuity of the film, as seen in Figure 1. Pt and ALD Ru had films with the smaller grains (> 100 nm), Au films had grains around 100 nm, and the various TiN substrates all produced the largest grains (< 200 nm). All samples showed a continuous film, except for the non-continuous TiN (TiN NC). TiN NC film had islands of Ru and a large variance in grain size. By using HF to remove the oxide layer on TiN before deposition, more nucleation sites occurred and the grain size became more uniform. TiN can grow a continuous film without HF (TiN C), but non-planar growth of the Ru can sometimes leave gaps and varying grain size.

Nucleation plays a part in the type of films produced. The ALD Ru surface produced a shiny film that had high performance. Because the Ru electrolyte was nucleating on a Ru substrate, the growth was most likely layer growth, which is smooth and continuous with fewer film defects. On the other substrates, Ru grew through a nucleation-coalescence mechanism, leading to a variety of grains and more defects in the film. ALD Ru pretreatment on the electrodes substrate could be a successful mechanism to improve the Ru electrochemical deposition. Ru electrochemical deposition is required in addition to ALD because it increases the thickness of the film to the desired level [6].

For the mechanical robustness of a probe film, a continuous film with small grains would most likely be best, but the CSC and impedance will further be tested to determine the film properties.

Characterization Methods:

Cyclic voltammetry (CV) can be used to identify the presence of reactions such as electron transfer, reduction and oxidation. Voltammograms, the graphs resulting from CV, provide information on the reversibility of reactions, quantity of electro-active material on the electrode and the stability of the electrode [7, 8]. CV was conducted with a three electrode set up using a potentiostat (CompactStat, Ivium Technologies), a Pt counter electrode, and a non-current carrying reference electrode AglAgCl [7]. It is standard to conduct CV scans at potentials between -0.6 and 0.8V for electrodes meant for biological applications, since it is important to stay within the water electrolysis window [1]. In this report, CV scans were performed for 3 or 10 cycles [7].

After initial CV scans it was seen that the shape and area of the curve significantly change after the first cycle. This possibly indicates that the surface is undergoing a sensitive irreversible reaction. To reduce this possibility, the potential window was decreased to -0.6 to 0.4 V.

Phosphate buffered saline (PBS) was chosen as the electrolyte for the CV scan and impedance testing because it is representative to the ion concentrations found in the body.

The cathodic charge storage capacity (CSC) is a quantitative assessment of a neural probe as a recording or stimulating device. The CSC is calculated using the results of a voltammogram using the following equation in Figure 2:

$$CSC = \frac{1}{vA}\int_{E_c}^{E_a} i dE \qquad \left[C \ \ cm^{-2}\right]$$

where v is the scan rate (V/s), A is the exposed surface area (cm^2), E is the electrode potential (V), E_a and E_c are the anodic and cathodic potential limits (V) and i is the measured current (A) [9].

Impedance is the quantification of a substrate's opposition to alternating current and is often used as another characterization method for neural probes. Probes require low impedance so charge can easily be transferred to or from the probe [10]. Most literature measures the impedance for frequencies between 10^{-1} to 10^5 Hz, but report impedances at 1 kHz for comparison. Impedance investigation is performed with a potentiostat (CompactStat, Ivium Technologies).

Characterization Results and Discussion:

Samples were initially CV scanned from -0.6 to 0.8 V but the scan window was adjusted to -0.6 to 0.4V after a peak indicating oxidation was seen as in Figure 3. The peak is not seen in scans from -0.6 to 0.4V. CV scans of Ru plated substrates show significantly more internal area than their blank substrate counter parts as seen in Figure 4. Additionally, between, each cycle, the voltammogram shape remains the same, but shifts vertically. Initial changes between the first and second cycles can be attributed to a sensitive reaction [7].

Charge storage capacity was calculated for all samples created and the CSC's of the best performing samples for each substrate and their blank standards are displayed in Figure 5. Au, TiN, TiN treated with HF, and ALD Ru all saw a significant increase in CSC after the deposition of Ru. Interestingly, Pt saw a decrease in CSC after the deposition of Ru, most likely due to strong gas evolution during plating.

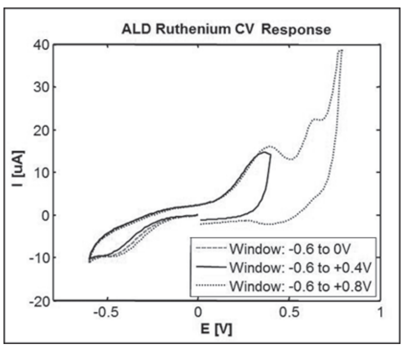

Figure 3: Cycle ranges and resulting voltammograms.

Sample	Electrolyte	Blank Substrate CSC (mC/cm^2)	Best Ru CSC (mC/cm^2)	CSC Percent Increase
Au	$RuCl_3$	0.12±0.1	1.2 ±0.3	900%
Pt	$RuCl_3$	1.0±0.1	0.81±0.07	-19%
ALD Ru	Ru	0.20±0.1	1.2±0.09	400%
TiN (C)	Ru	0.71±0.04	1.4±0.3	97%
TiN (NC)	Ru	0.71±0.04	1.6±0.1	125%
TiN HF	Ru	0.81±0.02	2.0±0.1	147%

Figure 5: The calculated CV with the percent increase from blank substrate.

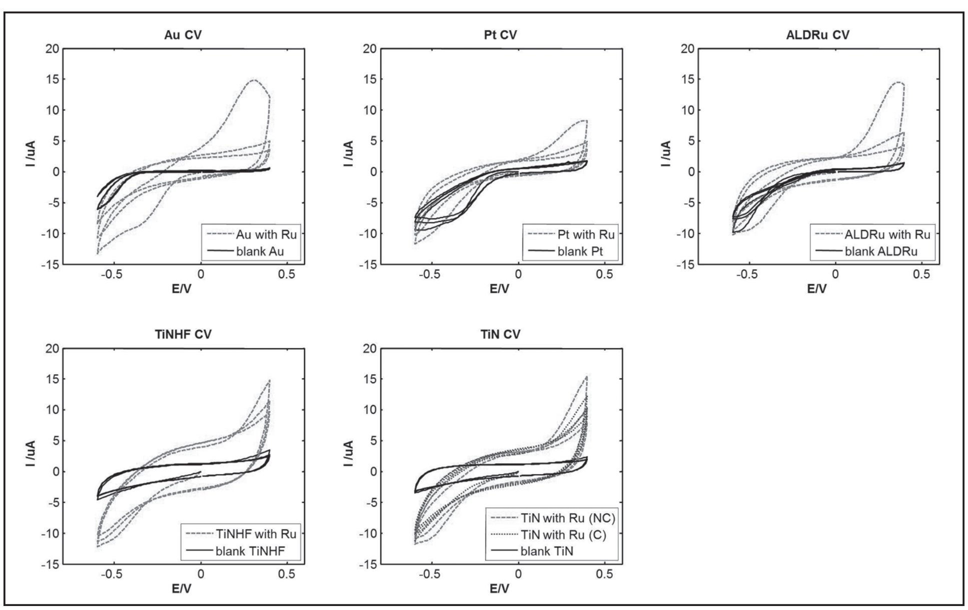

Figure 4: Voltammograms of samples compared to blank substrates.

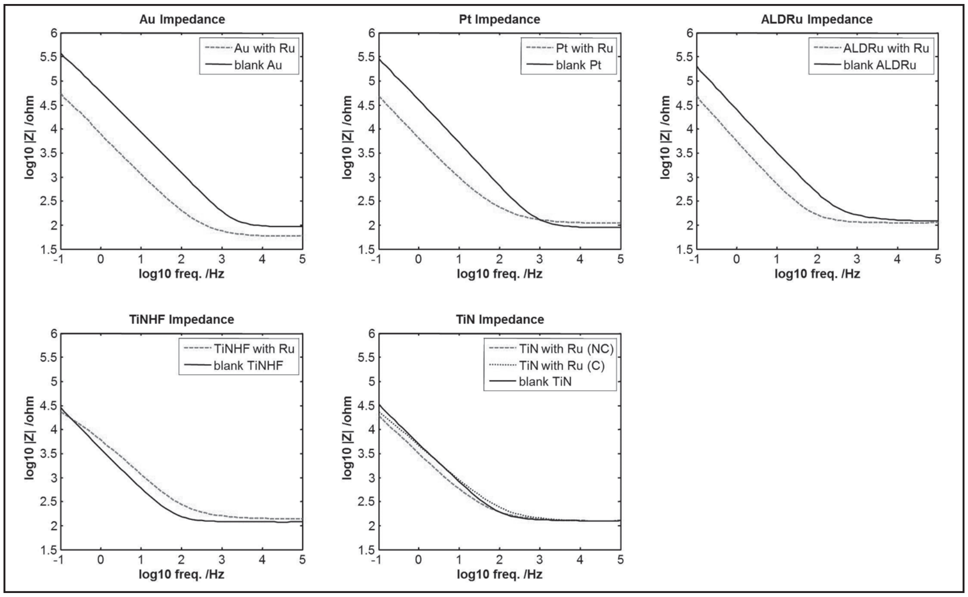

Figure 6: Impedance measurements as compared to the blank substrate.

Figure 6 indicates that Ru film on a substrate lowers the impedance at frequencies below 1 kHz. Above 1 kHz, Au, Pt, TiN treated with HF, TiN and ALD Ru all have very similar impedances of approximately 100 ohms.

All samples were characterized using these techniques, however, only the best performing samples for each substrate are shown in the figures.

Conclusions:

Electrochemically plating ruthenium increased the CSC values for all substrates except for Pt and decreased the impedance for all substrates except for TiN. Iridium oxide is the current high performance standard, but CSC values ranging from 2.8-45 mC/cm^2 [1, 2, 4, 12]. These values were calculated using various solutions and voltage windows, but provide a range to compare Ru films. The Ru films produced have a CSC ranging from 0.81 ± 0.07 to 2.0 ± 0.1 mC/cm^2. These results show that Ru might be useful for improving the electrical properties of electrode coatings, and would be best suited for Au, TiN, or ALD Ru probes. Further investigation to improve Ru coatings on Pt would allow for a broader application of Ru electrodes.

Acknowledgements:

We would like to thank the National Science Foundation, the National Nanotechnology Infrastructure Network International Research Experience for Undergraduates (NNIN iREU) Program, Lynn Rathbun, imec, Herc Neves, Alex Radisic, and John O'Callaghan.

References:

[1] Cogan, Annu. Rev. Biomed. Eng. 10 (2008) 275-309.

[2] Cogan, Troyk, Ehrlich, Plante, IEEE Trans. Biomed. Eng. 52 (2005) 1612-1614.

[3] Frölich, Rzany, Riedmüller, Bolz, Schaldach, J. Mat. Sci.: Materials in Medicine 7 (1996)393-397.

[4] Lu, Wang, Cai, Cao, Yang, Duan, Sensors and Actuators 137 (2009) 334-339.

[5] Galizzioli, Tantardini, Trasatti, J. of App. Electrochem. 4 (1974) 57-67.

[6] Paunovic, Milan, Mordechay Schlesinger, and Electrochemical Society. Fundamentals of electrochemical deposition. Wiley-Interscience, 1998. Print.

[7] Compton, Banks. Understanding Voltammetry. Singapore: World Scientific, 2007. Print.

[8] Pletcher, and Southampton Electrochemistry. Instrumental methods in electrochemistry. Chichester: Horwood Publishing, 2001. Print.

[9] Negi, Bhandari, Rieth, Solzbacher, Biomed. Mater. 5 (2010) 15007.

[10] Robinson, Davidson, Wright, Pomfrett, McCann, IEEE Eng. in Med. And Biol (2008) 1171-1174.

[11] Wang, Liu, Durand, IEEE Trans. Biomed. Eng. 56 (2009) 6-14.

[12] Mann, Freyland, Raz, Ein-Eli, Chem. Phy. Letts 460 (2008) 178-181.