Development of Titanium Nitride Fractal Coatings for Cardiac and Neural Electrostimulation Electrodes

C.A. Outten, D.W. Konopka, and T.F. Fennessey, Denton Vacuum, Inc., Moorestown, NJ

ABSTRACT

This work deals with the development of reactively sputtered fractal titanium nitride coatings for use in electrostimulation and recording electrodes. Electrical stimulation of cardiac and nerve tissues is an active area of research. This presentation will focus on the process development and characterization of porous, columnar titanium nitride coatings that exhibit high electrochemically active surface areas. Depositions were conducted in an industrial-scale sputtering system with substrate temperature varying between 25 – 130°C. Low-temperature deposition of high surface area coatings is presented. These coatings are of particular interest for stimulation electrodes where dimensional stability is a concern, for example implantable neural prostheses leads. The coating microstructure was investigated with Focused Ion Beam Microscopy. These results were used to assess the impact of substrate temperature on film porosity and grain size. The electrical performance of these coatings was analyzed with Electrical Impedance Spectroscopy (EIS) to quantify the electrochemical vs. geometrical surface area, charge injection capacity, and charge storage capacity. The stress evolution of these films was measured real-time with an *in situ* stress monitoring system and compared to *ex situ* stress measurements.

INTRODUCTION

Fractal titanium nitride (TiN) thin films are used to improve the performance of electrostimulation and recording electrodes for cardiac and neural prostheses and treatments. Titanium nitride is an ideal material for these applications due to its electrical conductivity, chemical stability, and biocompatibility [1]. The fractal nomenclature refers to a porous coating with an extremely large ratio of electrochemical surface area (ESA) to geometrical surface area (GSA) [2]. This surface morphology results in an electrode with high charge transfer when implanted in cardiac or nerve tissue. Typically, these coatings are DC reactively sputtered in nitrogen (N_2) and argon (Ar) gas mixtures at substrate temperatures of 200 – 400°C [3]. For this study, the motivation was to develop fractal TiN coatings for emerging neural and cardiac devices that are fabricated on temperature sensitive substrates, ex. polymers, or require micro-patterning, ex. intracortical microprobes or neural microelectrodes arrays [1].

EXPERIMENTAL PROCEDURES

Fractal TiN films were deposited using DC reactive magnetron sputtering from a titanium (Ti) (99.99 % purity) target on silicon wafers and titanium test electrodes (16 mm-dia.). The Ti targets were 3.0-inch (76 mm) in diameter and mounted on a circular, planar magnetron. The magnetrons were mounted on a vacuum sputtering system (Denton Vacuum Explorer) that was evacuated to a base pressure of 10^{-7} Torr by a turbomolecular pump. A photograph of the sputtering system is shown in Figure 1.

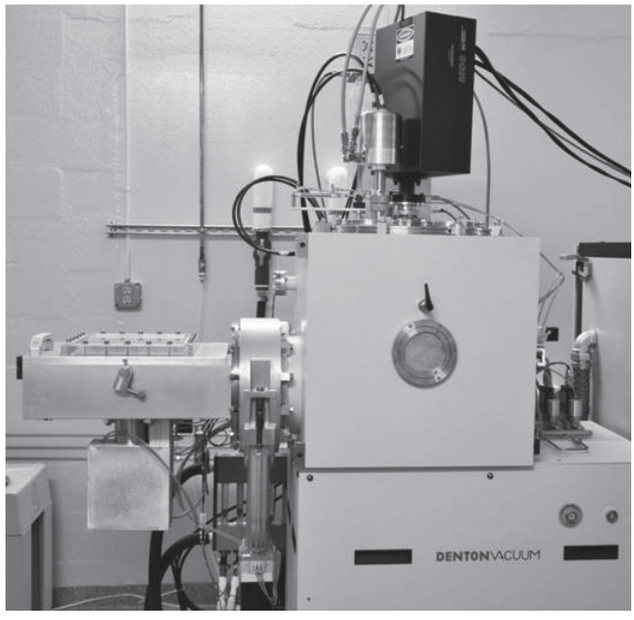

Figure 1: Photograph of the magnetron sputtering system with an in situ *multi-beam optical sensor.*

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Substrates were mounted on a rotating fixture that could be simultaneously biased and heated. The substrate bias was provided by a 13.56 MHz radio frequency power supply and matching network. Substrate heating was provided by a temperature controlled resistive heater. Substrates were loaded into sputtering chamber through a load-lock with automated transfer.

Several techniques were utilized to characterize the microstructure, electrochemical performance, and stress behavior of as-deposited TiN films. The surface morphology and microstructure were characterized with Focused Ion Beam (FIB) microscopy. Film thickness was measured with a surface profilometer and correlated with FIB cross-sectional micrographs. Cross-sectioned electrodes were coated *in situ* with a relatively thick, smooth platinum film to planarize the surface prior to imaging. This technique is employed to reduce scattering from high topology surfaces and to improve the resolution of nanoscale features. The electrical performance of coated Ti electrodes was measured with cyclic voltammetry, impedance spectroscopy, and potential transient analysis in buffered phosphate saline (PBS) solutions. These *in vitro* characterizations simulate *in vivo* conditions for implanted cardiac and neural electrostimulation electrodes.

The stress evolution of films was monitored real time during deposition using a Multi-beam Optical Sensor (MOS) developed by k-Space Associates, Inc. This sensor revealed real-time evolution of film stress. The MOS sensor hardware was mounted on top of the vacuum chamber and precisely aligned to the center of the rotation fixture as shown in Figure 1. *In situ* stress measurements were performed on polished silicon wafers.

RESULTS AND DISCUSSION

Surface Morphology

The surface morphology of as-deposited fractal TiN films was examined by FIB at different substrate temperatures. All of the coatings were deposited on titanium electrodes to a thickness of 2.5- 3.0 μm. The depositions were carried out in an Ar and N_2 gas admixture at a cathode power density of 0.16 Watt/mm^2 (103 Watt/in^2) and a working pressure during sputtering of 6 mTorr. FIB micrographs, plan-view and cross-sectional images, are presented in Figure 2(A) – (F) for fractal TiN deposited at three different substrate temperatures (T_s): (A) 25^{o}C; (B) 80^{o}C; and (C) 130^{o}C, respectively.

In the plan-view images, Figures 2 (A) - (C), the micrographs reveal a highly textured surface topology with extended voids along grain boundaries. Chawla et. al. reported a similar surface morphology for nanocystalline TiN films deposited at T_s < 450^{o}C [4]. In addition, it is seen that TiN grains are strongly faceted and exhibit a triangular morphology. This textured morphology is a consequence of a preferred (111) crystallographic orientation of the grains. At low substrate temperatures, adatom mobility is low and the (111) orientation is energetic favorably in face-centered cubic materials, such as TiN [5]. The TiN grains consist of a dense array of nano-sized faceted clusters that are 100-200 nm in diameter for the deposition conditions examined in this study. The surface analysis indicates that the coating microstructure consists of highly columnar TiN pillars with dendrite-like pores extending perpendicular to the film. There was no change observed in the grain structure between 25^{o}C- 130^{o}C. Similar results were reported in metallic and nitride films deposited at low deposition temperatures [6, 7].

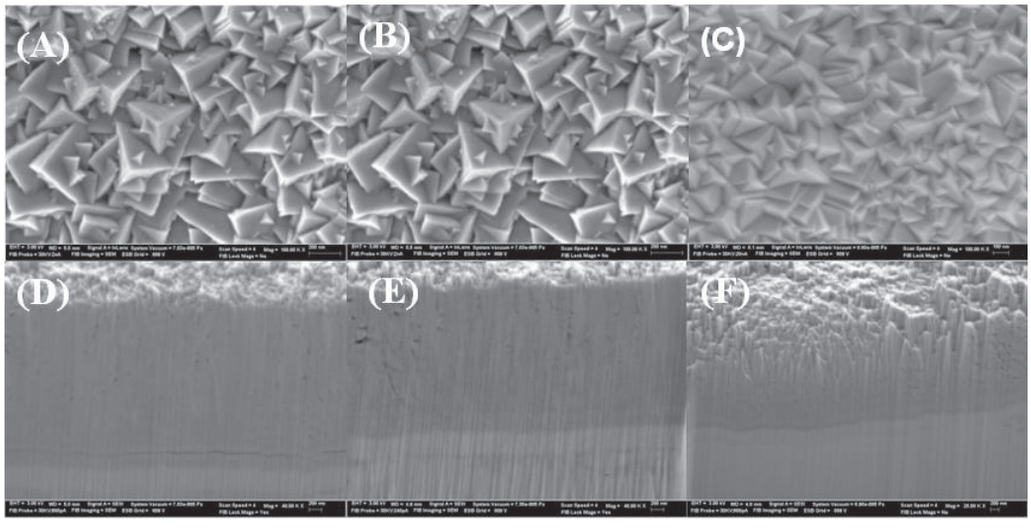

Figure 2: Focused Ion Beam micrograph- plan-view (top) and cross-section (bottom) of fractal TiN films deposited at (A & D) 25^{o}C; (B & E) 80^{o}C; and (C & F) 130^{o}C.

Micrographs of the cross-sectioned electrodes are shown in Figures 2(D) - (F). In each micrograph, the columnar structure is clearly visible along with dense network of nano-scale, highly oriented pores normal to the substrate. The interface between the Ti electrode surface and TiN coating is sharp and distinctive. The columns are highly oriented vertical to the surface of the electrode and extend through the entire thickness of the coating. Based on the FIB results, the as-deposited TiN coatings are expected to provide very large the ESA/GSA ratios and hence a significant enhancement of charge injection as compared to an uncoated Ti electrode. Electrochemical analyses were conducted on TiN coated electrodes to validate this hypothesis.

In Vitro Characterization

Electrochemical characterization was performed to quantify the charge storage capacity (CSC) and charge injection capacity (CIC) of the previously described TiN coated electrodes. One of the deposition conditions from the FIB analysis was selected. Specifically, a 2.5 µm-thick, TiN coating deposited on a Ti electrode at 25°C was selected for characterization. The electrode was coated with a 3 µm-thick parylene-C to electrically isolate the test area. A 50 µm-dia. opening in the parylene was etched by oxygen plasma to expose the test area. The electrode was soaked in a PBS solution to perform electrochemical impedance characterization. The measurements were performed with an Ag/AgCl reference electrode and Pt counter electrode.

In Figure 3, the cyclic voltammagram (A) and potential transient response (B) of the TiN coated electrode are presented. The charge storage capacity was calculated to be 223.6 mC/cm^2 by integrating the area under the cyclic voltammagram. The charge injection capacity was determined to be 0.8 mC/cm^2 based on the voltage response when a 0.4 msec pulse was applied to the electrode. For reference, an uncoated Ti electrode was measured using on the identical procedure. An uncoated Ti electrode was measured to have a CSC of 1.9 mC/cm^2 and CIC of 0.02 mC/cm^2. As anticipated, the TiN coated electrode delivered a significant improvement in both charge injection and charge storage. Weiland et. al. performed similar *in vitro* testing on porous, sputtered TiN coatings and reported CSC and CIC values of 2.35-2.47 mC/cm^2 and 0.87-0.9 mC/cm^2, respectively [8]. Cogan discussed that the pore resistance imposes a geometric limitation on the charge-injection capacity [1]. For porous TiN, Cogan reports that the theoretical maximum CIC to be 1 mC/cm^2 based on double-layer faradic charging models. In the case of the charge storage capacity, theoretical modeling has proven problematic due to the inability to quantify pore resistance and capacitance. Hence, further study is required to understand why the measured CSC is significantly higher than Weiland's results.

In Situ Stress Measurements

In situ stress measurements were performed on 50 mm (2-inch)-dia. polished silicon wafers using the MOS system. The motivation was to understand the impact of key deposition parameters- for example substrate bias, working pressure, substrate temperature, magnetron power- on as-deposited film stress. It has been reported that film stress is a critical material property in the design of micro-electrode probes and arrays for neural stimulation applications [9]. These neural probes are fabricated on thin metal or polyimide substrates where stress-induced curvature of the devices is a concern.

Preliminary data on the stress evolution of low-temperature, fractal TiN coatings is presented in Figure 4. The depositions conditions were similar to those reported earlier in this work on Ti electrodes: cathode power density of 0.16 Watt/mm^2 (130 Watt/in^2) and the sputtering pressure of 6 mTorr. The wafer curvature was measured in a Dektak 150 profilometer pre and post deposition for *ex situ* stress measurement. The

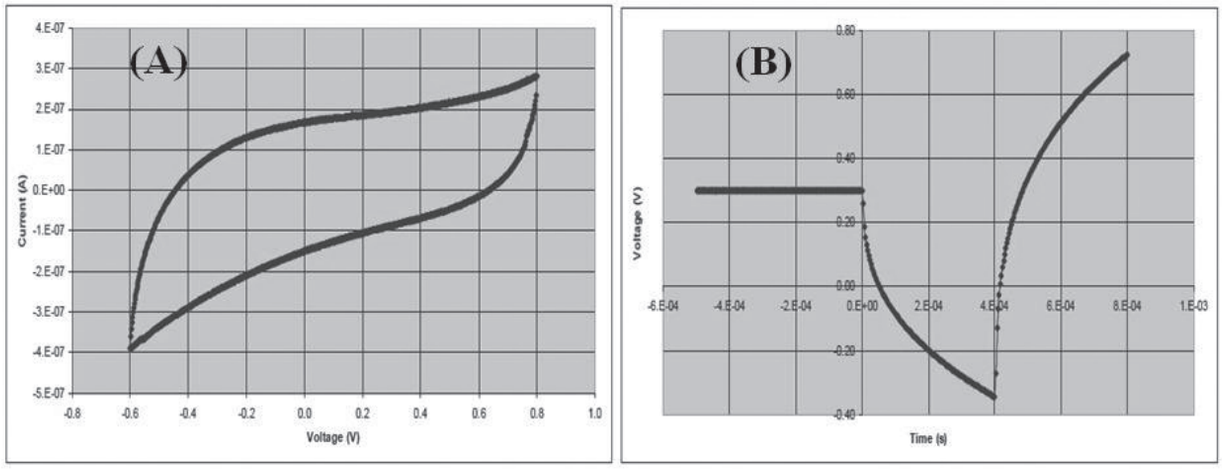

Figure 3: (A) Cyclic voltammagram and (B) Potential transient when 0.4-msec pulse was applied to fractal TiN coated electrode.

TiN film was deposited to a thickness of 6.175 µm. In Figure 4, it is observed that the substrate curvature increases linearly after the start of the deposition to a value of 0.08 m^{-1}. Stoney's equation was used to calculate the fractal TiN film stress [10]. The intrinsic film stress was determined to be +47 MPa (tensile). Post deposition, the substrate was allowed to cool under vacuum chamber (in 10^{-7} Torr range). The wafer curvature increased rapidly to 0.13 m^{-1} as shown in Figure 4. This behavior is attributed to a thermally induced stress during cooling. The total film stress was calculated by adding the intrinsic stress and the thermally induced stress. The total *in situ* stress was calculated to be +72 MPa (tensile).

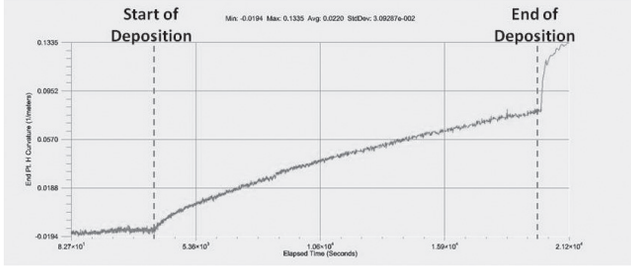

Figure 4: In-situ *measurement of wafer curvature as a function of time.*

The abrupt change in wafer curvature was unexpected, but may allow a clear differentiation of intrinsic stress from thermally induced stress. Chason remarked that the rapid change in curvature during cool down is related to the relaxation of film stress by diffusion of atoms out of grain boundaries [11]. However, the source of this relaxation is still being debated. It is not known if the columnar and porous microstructure of these films is a contributing factor. Due to the difficulty of modeling both stress and diffusion in porous materials, it was decided to corroborate these results experimentally. A Dektak 150 profilometer with a stress software package was employed to perform *ex situ* stress measurements.

The TiN coated wafer was removed from the sputtering system after cooling to room temperature. The curvature of the wafer was measured on the Dektak 150 in the identical locations as the pre-deposition measurements. The film stress was calculated using the pre- and post-wafer curvature measurements and Stoney's equation [10]. The *ex situ* film stress was calculated to be ~ +67 MPa (tensile). The *ex situ* stress measurement was in good agreement with the *in situ* MOS stress data. More work is in progress to characterize the stress evolution of fractal TiN coating during deposition. The goal of these studies is to minimize the stress in these coatings for applications where dimensional stability is critical, ex. on flexible substrates.

CONCLUSIONS

This work has shown that fractal TiN coatings can be deposited by DC magnetron sputtering at low substrate temperature which possess both high charge injection and charge storage capacity. The coatings' porous, columnar microstructure creates high-surface area electrodes with greatly enhanced electrochemical activity that is ideal for electrostimulation applications. *In situ* stress measurements provide insight into the stress evolution of these films and the ability to tailor the film stress during deposition. All of these factors open new opportunities for fractal TiN in emerging neural and cardiac implantable devices and electrostimulation therapies.

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