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TiN Coatings on Titanium Substrates Using Plasma Assisted Ion Implantation

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Abstract. We present results on producing TiN coatings on titanium substrates, using Plasma-Based Ion Implantation and Deposition (PBII&D). In PBII&D the substrate is immersed into stationary plasma which contains the ion species to be implanted. A negative high voltage pulse is applied to the substrate, which causes the ions in the ion sheath surrounding the substrate to be accelerated across the sheath and implanted into the substrate. We have used a 13.6 MHz, 70 W, radio frequency (RF) plasma, produced with a mixture of 80% N_2 + 20% H_2, at 200 mTorr, with 4 kV, ≈10 μs pulses, at a 0.2 kHz rate. During the implantation process the titanium substrate is heated at 400° C range. The resulting TiN coatings are characterized using atomic force microscopy (AFM), x-ray diffraction (XRD), and Vickers hardness test. Optical emission spectroscopy (OES) is used to identify characteristic RF plasma species.

1. Introduction

Titanium is widely used in biomedical application [1, 2]. Because titanium by itself it is not a fully biocompatible material, it requires a biocompatible coating to be suitable for more critical requirements [3, 4]. Besides their well-known properties of hardness, TiN coatings exhibit better biocompatibility features than those of bared titanium. This feature has stimulated research aiming to improve on TiN coatings properties, such as roughness, deepness and adhesion [5, 6]. Different plasma based techniques, such as inductively coupled plasma assisted physical vapor deposition [7], reactive plasma spraying [8], or direct current magnetron sputtering [9], have been used to produce TiN coatings Plasma-Based Ion Implantation and Deposition (PBII&D) is a well-developed technique which allows deep implantation of ions into a substrate [10, 11]. The substrate is immersed into stationary plasma which contains the ion species to be implanted. When a negative high voltage pulse is applied to the substrate, ions in the ion sheath surrounding the substrate are accelerated across the sheath and implanted into the substrate. Successful implantation depends critically on high voltage pulsing parameters (1-100 kV, 1-50 μs, 10-1000 Hz repetition rate). The implantation voltage determines the characteristic depth of the implanted ions, the average implanted ion dose per pulse depends on pulse length, and the repetition rate defines the exposure time required to achieve a given implantation profile. We have previously reported on the synthesis of sub-micron size carbon structures using a combination of 13.6 MHz radio frequency (RF) plasma and PBII&D, operating at 30 W, with 4 kV, 2 μs pulses, at a 2 kHz rate [12]. In order to explore different parameter regimes and

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aiming to improve on TiN coatings, we have conducted preliminary experiments to produce and characterize TiN coatings on Titanium substrates, using PBII&D techniques in RF plasmas.

2. Experimental set-up

The experiments are conducted using a capacitively coupled RF plasma generator at 13.6 MHz, operating at 70 W, and produced with a mixture of 80% N_2 + 20% H_2, at 200 mTorr working pressure. Nitrogen flow rate was fixed at 13 sccm. The use of a nitrogen-hydrogen mixture is motivated by the fact that at substrate temperatures around 400°, addition of hydrogen in the range 5-50% results in an increased nitride layer, provided that the partial pressure of nitrogen is maintained [13]. As substrate, we used a flat, polished Titanium (TI007945) sample. In a pre-implantation treatment the substrate is exposed to argon plasma at 200 mTorr, for 15 min, in order to improve surface cleanness. During the implantation process the substrate temperatures is maintained at 400°C. Implantation time is kept at 60 min.

PBII&D is performed with an applied negative biasing up to 10 kV, at 0.2 kHz, with ≈10 μs pulse width. The high voltage driver is based on a combination of ferrite core pulse transformers and insulated gate bipolar transistors (IGBT). In present experiments the high voltage pulser was used at 40% of the nominal highest voltage output, in order to protect from eventual breakdown to the RF electrodes. Figure 1 shows a characteristic high voltage pulse, as used in the experiments.

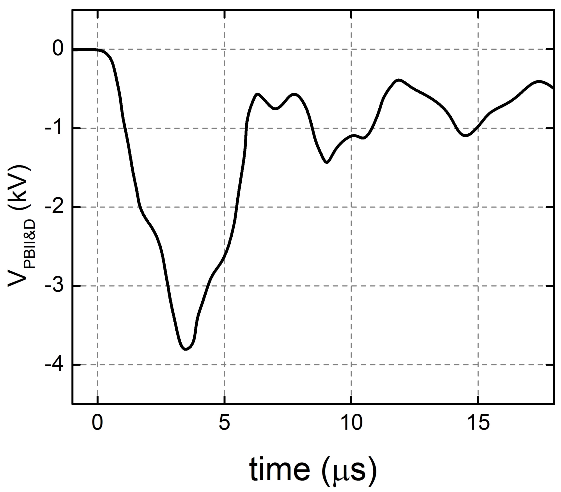

Figure 1. Characteristic high voltage pulse used in the PBII&D process.

The implanted substrates are characterized using atomic force microscopy (AFM), x-ray diffraction (XRD), and Vickers hardness test. Optical emission spectroscopy (OES) is also used to identify dominant species in the RF plasma.

3. Results and Discussion

Figure 2 shows a characteristic emission spectrum of the stationary RF plasma, obtained with a low resolution Ocean Optics PC2000 spectrometer. The strongest emission lines correspond to atomic hydrogen emission, H_α and H_β, together with neutral atomic and molecular nitrogen, and singly ionized nitrogen molecules. Weaker emission from single ionized nitrogen atoms can also be identified. As expected for a low pressure, low power RF plasma, with characteristic electron temperature around 1 eV, emission from neutral species becomes dominant. This fact precludes a clear observation of emission lines corresponding to single ionized nitrogen, as they either coincide with strong molecular bands, or merge with background noise.

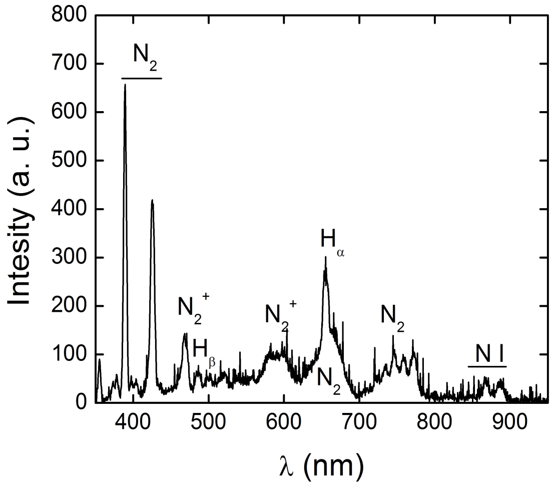

Figure 2. Optical emission spectroscopy of the RF plasma.

The effect on titanium surfaces due to RF plasma exposure, combined with negative high voltage pulsing, was investigated using a NanoWizard 3 NanoScience AFM. Figure 3 shows AFM images of the titanium surface, before and after the PBII&D process. The substrate temperature was kept at 400° during the implantation process. Surface roughness of implanted surfaces is seen to increase by up to a factor of ten, when compared with the unexposed surface. The observed roughness is similar to that reported in previous investigations of titanium nitride synthesized by dynamic nitrogen and titanium PBII&D, using a vacuum arc source for the titanium plasma and a hot filament glow to sustain the nitrogen plasma [14].

Vickers hardness tests at low load, $\approx 10\ gf$, indicate that surface hardness is around 3 times that of unexposed substrates, whereas at $\approx 100\ gf$ it becomes comparable to the unexposed titanium surface. A characteristic implanted layer thickness of around 300 nm is inferred from the Vickers test.

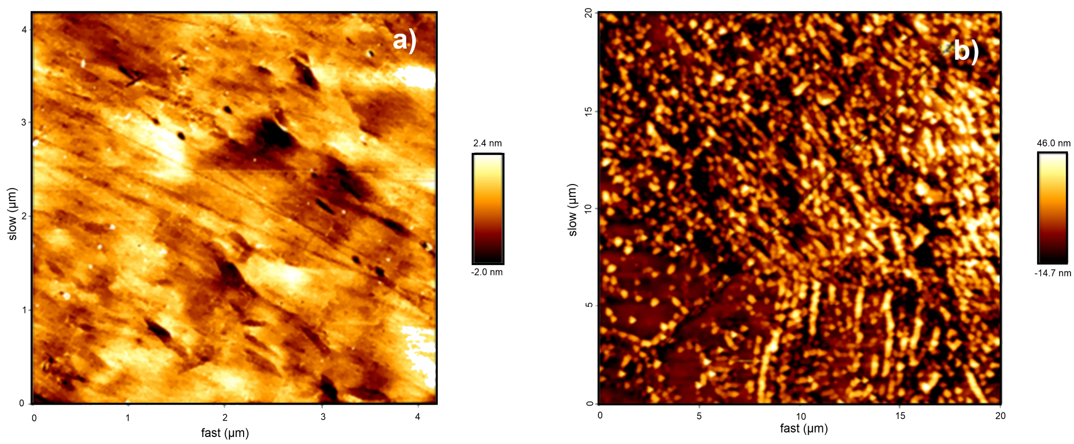

Figure 3. AFM images of, a) Titanium substrate before implantation, and b) substrate surface after PBII&D process.

XRD analysis was performed for different exposed samples, using a Bruker D8 Advance diffractometer. Figure 4 shows the XRD spectrum corresponding to the same exposed sample with an AFM image in figure 3-b. Data analysis of the x-ray diffraction pattern allows to identify distinctive peaks corresponding to TiN and titanium, and also some evidence of titanium oxide. This last, probably due to surface oxidation of previously unexposed substrate, which is not removed by the initial argon plasma treatment. The XRD data hints that a thin surface layer of mixed composition is formed as a result of the PBII&D process.

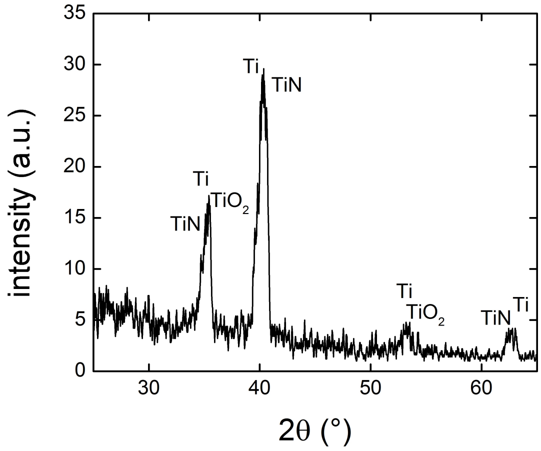

Figure 4. XRD spectrum of exposed sample.

4. Conclusions

Our preliminary results show the feasibility of implanting nitrogen ions onto a titanium substrate using a combination of RF nitrogen plasma and PBII&D techniques. Standard surface science diagnostics indicate that the process results in a sub-micron thickness layer, partially composed of titanium nitride, with improved hardness, as compared with unimplanted samples. Further parametric studies are being performed, in order to optimize the process, together with a more comprehensive characterization of both, the resulting titanium nitride coatings and the RF plasma features.

Acknowledgments

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